

The Electron Energy Loss Rates by Polar Molecules

By

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Synopsis: Simple useful formulae are derived for rates of electron energy loss through the rotational and vibrational excitation of polar molecules. Accuracy of these formulae is tested by comparing rates from the formulae with results of direct numerical calculations from the relevant cross sections on some molecules abundant in the cometary atmospheres. The energy loss rates, as functions of the difference between electron and gas temperatures, are presented in graphical forms for H₂O, OH, CO, CH, NH, NH₃, and also for H₂ and O for the gas temperatures: 300K, 500K and 1000K.

1. INTRODUCTION

Accurate cooling rates of the electron gas interacting with atoms and molecules in gases are required in quantitatively understanding the energetics of ionized gases in the planetary and space physics and also the relaxation of the electron temperature in laboratory experiments.

Thermal electrons in a gas lose energy through the interactions with atoms and molecules and often with charged particles in the gas if the electron temperature T_e is above the gas temperature T_g . Very often, excitations of the molecular rotation and vibration are the most efficient energy loss mechanisms for the thermal electrons in a gas of low ionization degree as compared with the other kinds of collisions: momentum transfer, fine-structure excitation, electronic excitation and ionization.

The fundamental theory of the electron-ion interaction has been discussed repeatedly in the past and an expression for the rate of the energy transfer between electrons and ions in ionized gases is known to an accuracy sufficient for practical applications [1]. However, in the case of the electron energy loss resulting from the collisions with neutral particles the situation is not so satisfactory, owing to a variety of relevant interactions (long-range multipole interactions, polarization force, short range interaction, and exchange force) and sometimes to the greatness of the number of energy levels involved. Only to some individual atoms and molecules, analytical expressions have been presented to approximately reproduce the numerically calculated values.

The energy loss rate for the rotational excitation of the diatomic molecule through a quadrupole interaction was given by Mentzoni and Row [10] using the Gerjuoy-Stein [3]'s cross section; i.e.,

$$\frac{1}{n} \frac{dT_e}{dt} = -0.905 \times 10^{-6} Q^2 \cdot B (T_e - T_0) / T_e^{1/2}, \quad \text{°K} \cdot \text{cm}^3 \cdot \text{sec}^{-1} \quad (1)$$

where Q is the quadrupole moment in unit of ea_0^2 ($-e$ is the electron charge, $a_0 = 5.292 \times 10^{-9}$ cm is the Bohr radius), and B is the rotational constant of the molecule in eV. Since then, this formula has been frequently used in aeronomical problems. But a care must be taken in the actual applications of this formula. Sometimes it gives a result considerably deviated from more accurate values when the electron temperature becomes high. This is due to the preponderance of the short range forces over the quadrupole interaction. Thus we had better, in general, use an "effective" quadrupole moment for Q in the expression (1).

When we study the planetary or astrophysical problems, the electron energy loss rate due to other kinds of interactions with gas molecules is needed. In the interstellar matter, there are a large number of polar molecules, which are very efficient to cool electron gas. We try to derive in this paper some useful formulae for the rotational and vibrational energy loss rates for electrons in polar gases.

2. GENERAL FORMULAE

2.1 Rotational excitation of linear or symmetric-top molecules

The mean cooling rate for thermal electrons (in Maxwellian velocity distribution) through the rotational excitation and de-excitation of symmetric-top molecules will be expressed as follows

$$\frac{1}{n} \frac{dT_e}{dt} = -\frac{2}{3\kappa} \left(\frac{m_e}{2\pi\kappa T_e} \right)^{3/2} \frac{8\pi}{m_e^2} \sum_{J,K} \Delta E_{J,K \rightarrow J+1,K} \times \int_*^\infty dE \cdot E e^{-E/\kappa T_e} \\ \times \{ \sigma(J, K \rightarrow J+1, K; E) n_{J,K} - \sigma(J+1, K \rightarrow J, K; E) n_{J+1,K} \} \quad (2)$$

where the meaning of quantities involved is as follow: m_e , electron mass; κ Boltzmann constant; J , total angular momentum of the molecule before collision; K , projected component of J upon the symmetry axis of the molecule; $\sigma(J, K \rightarrow J+1, K; E)$, cross section for the transition $(J, K) \rightarrow (J+1, K)$; $n_{J,K}$, population of a state (J, K) normalized such that $\sum_{J,K} n_{J,K} = 1$; $\Delta E_{J,K \rightarrow J+1,K}$, absolute value of the energy difference between two states (J, K) and $(J+1, K)$. As the symmetric-top molecule has a dipole moment parallel to the symmetry axis, no transitions on K is introduced through the dipole interaction. The lower limit of the integral in (2) is $\Delta E_{J,K \rightarrow J+1,K}$ for the excitation term and zero for the de-excitation term.

The cross sections for the excitation and de-excitation processes are, respectively, given by Itikawa[7], as follows

$$\sigma(J, K \rightarrow J+1, K) = \frac{8\pi}{3k^2} D^2 \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \ln \left| \frac{k+k'}{k-k'} \right| \\ \sigma(J, K \rightarrow J-1, K) = \frac{8\pi}{3k^2} D^2 \frac{J^2 - K^2}{J(2J+1)} \ln \left| \frac{k+k''}{k''-k} \right|, \quad (3)$$

where k is the wave number of electron before collision, D is the dipole moment of the molecule, k' , k'' are the wave numbers after excitation and de-excitation collisions, respectively. These formulae are based on the Born approximation. It must be noted that the Born approximation for the rotational transitions through the dipole interaction has still fair validity at low electron energy range, since a greater part of contributions to the cross section comes from distant encounters[15]. This will probably make the electron energy loss rate based on the Born approximation more reliable for polar molecules than for non-polar molecules. The construction of the energy loss rate in an analytical form for the rotational transitions is possible through the use of the Born cross sections (3) which are of very simple forms for the general quantum numbers J and K .

Using the well-known expression for the energy level*)

$$F(J, K) = BJ(J+1) + (A-B)K^2, \quad (4)$$

the normalized level population is expressed as

$$n_{J,K} = (2J+1)g(J, K) \exp(-F(J, K)/\kappa T_g) / N, \quad (5)$$

where

$$N = \sum_{J,K} (2J+1)g(J, K) \exp(-F(J, K)/\kappa T_g),$$

A and B are the rotational constants, $g(J, K)$ is the statistical weight other than $(2J+1)$ of the level (J, K) , and T_g is the rotational temperature of the molecules.

The factor $g(J, K)$ will be discussed next. The states $K \neq 0$ are doubly degenerate while the states $K=0$ are not. In addition, those symmetric-top molecules where two of their principal moments of inertia are not accidentally equal, will have a p -fold axis of symmetry in general (p is an integer). They produce a statistical weight in an involved way, corresponding to nuclear spin I and its statistics (Bose-Einstein or Fermi-Dirac). $g(J, K)$ is also related whether K is a multiple of p or not, and to the parity of K . Besides, the case $K=0$ often has to be handled separately. In any way, the statistical weight is periodically changed, so that the effect of variation of $g(J, K)$ to the cooling rate will be smoothed out if there are a large number of rotational states involved. This is the case if T_g is not too low. Under the same circumstance, the special behavior of the $K=0$ level does not give any appreciable effect. Therefore, we shall assume that $g(J, K)$ is independent of J, K on the average in deriving the analytical formula. In the direct numerical calculations in §3 to test the analytical formula, these weights are rigorously taken into account.

The preceding story will be reduced to the case of the diatomic molecules in a limit $A \rightarrow \infty$. Then the quantum number K means a projection upon

*) The correction due to the centrifugal stretching is exceedingly small at rotational temperature of our interest.

the molecular axis of the sum of electronic orbital and spin angular momenta. In a $^1\Sigma$ state, K is zero and only a single rotational sequence exists, while for a $^2\Pi$ state (as in OH, CH, etc.) two sequences exist ($K=1/2, 3/2$).

From (2) and (3), we obtain

$$\begin{aligned} \frac{1}{n} \frac{dT_e}{dt} = & -319.6 \frac{D^2}{T_e^{1.5}} \sum_{J=0}^{\infty} \sum_{K=0}^J \Delta E_{J,K \rightarrow J+1,K} \\ & \times \left[\frac{(J+1)^2 - K^2}{(J+1)(2J+1)} n_{J,K} \int_{\Delta E_{J,K \rightarrow J+1,K}}^{\infty} dE e^{-\beta E/T_e} \ln \frac{(\sqrt{E} + \sqrt{E - \Delta E_{J,K \rightarrow J+1,K}})^2}{\Delta E_{J,K \rightarrow J+1,K}} \right. \\ & \left. - \frac{(J+1)^2 - K^2}{(J+1)(2J+3)} n_{J+1,K} \int_0^{\infty} dE e^{-\beta E/T_e} \ln \frac{(\sqrt{E} + \sqrt{E + \Delta E_{J,K \rightarrow J+1,K}})^2}{\Delta E_{J,K \rightarrow J+1,K}} \right] \end{aligned} \quad (6)$$

where $\beta = 1.16049 \times 10^4$ is a numerical factor for unit conversion, D is in unit of debye, ΔE , A , and B are in eV. Abbreviating $\Delta E_{J,K \rightarrow J+1,K}$ as Δ , and putting $c = \beta/T_e$, the relevant integrals become

$$\begin{aligned} \int_{\Delta}^{\infty} dE e^{-cE} \ln \frac{(\sqrt{E} - \sqrt{E - \Delta})^2}{\Delta} = & e^{-c\Delta} \left[\int_0^{\infty} dx e^{-cx} 2 \ln(\sqrt{x + \Delta} + \sqrt{x}) \right. \\ & \left. - \ln \Delta \int_0^{\infty} dx e^{-cx} \right], \end{aligned}$$

and

$$\begin{aligned} \int_0^{\infty} dE e^{-cE} \ln \frac{(\sqrt{E} + \sqrt{E + \Delta})^2}{\Delta} = & \int_0^{\infty} dx e^{-cx} 2 \ln(\sqrt{x + \Delta} + \sqrt{x}) \\ & - \ln \Delta \int_0^{\infty} dx e^{-cx}. \end{aligned} \quad (7)$$

Integrating by parts

$$\int_0^{\infty} dx e^{-cx} \ln(\sqrt{x + \Delta} + \sqrt{x}) = \frac{\ln \Delta}{2c} + \frac{1}{2c} \int_0^{\infty} e^{-cx} \frac{dx}{\sqrt{x(x + \Delta)}}, \quad (8)$$

and utilizing the formula

$$\int_0^{\infty} e^{-cx} \frac{dx}{\sqrt{x(x + \Delta)}} = e^{c\Delta/2} K_0(c\Delta/2), \quad (9)$$

where K_0 is the modified Bessel function of the second kind, we obtain

$$[] \text{ in (6)} = \frac{(J+1)^2 - K^2}{J+1} \left(\frac{n_{J,K}}{2J+1} e^{-c\Delta} - \frac{n_{J+1,K}}{2J+3} \right) e^{(c\Delta/2)} \frac{1}{c} K_0(c\Delta/2). \quad (10)$$

With the use of (5)

$$[] = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} n_{J,K} \frac{1}{c} e^{-c\Delta/2} K_0(c\Delta/2) \{1 - e^{\beta\Delta(T_e - T_0)/(T_e T_0)}\}, \quad (11)$$

where Δ is $2B(J+1)$. Generally, the exponent in the last factor is very small

for the most important J 's which are specified by the rotational temperature. Thus

$$[\] = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} n_{J,K} e^{-c\Delta/2} K_0(c\Delta/2) \Delta(T_e - T_g) / T_g. \quad (12)$$

Using these expressions, we now have

$$\frac{1}{n} \frac{dT_e}{dt} = -319.6 D^2 \frac{(T_e - T_g)}{T_e^{1.5} T_g} \frac{1}{N} \sum_{J=0}^{\infty} \sum_{K=0}^J \frac{(J+1)^2 - K^2}{J+1} \Delta^2 \times e^{-\beta F(J,K)/T_g} \cdot e^{-c\Delta/2} K_0(c\Delta/2). \quad (13)$$

For $z \rightarrow 0$, K_0 behaves as $K_0(z) = -\ln(z/2) - \gamma + O(z \ln z)$, where γ is the Euler's constant ($=0.5772$). This relation can be applied here since $c\Delta/2 = \beta B(J+1)/T_e$ is a small quantity. Thus we have

$$e^{-c\Delta/2} K_0(c\Delta/2) \cong -\ln(cB(J+1)/2) - \gamma.$$

For further simplification of calculations, we now define the new quantities δ , ε , and ξ , and regard the discrete variables K and J to be continuous variables ($K \rightarrow x$, $J \rightarrow y$).

$$\delta = cB/2 \cdot e^{\gamma} \quad (\delta > 0), \quad \varepsilon = \beta(A-B)/T_g, \quad \xi = \beta B/T_g \quad (\xi > 0). \quad (15)$$

Then eq. (13) becomes

$$\frac{1}{n} \frac{dT_e}{dt} = 319.6 D^2 \frac{(T_e - T_g)}{T_e^{1.5} T_g} \frac{1}{N} 4B^2 \int_0^{\infty} dy \int_0^y dx [y^3 \ln(\delta y) e^{-(\varepsilon x^2 + \xi y^2)} - y x^2 \ln(\delta y) e^{-(\varepsilon x^2 + \xi y^2)}]. \quad (16)$$

We interchange the orders of the integrations and integrate first over y . The result is

$$\frac{1}{n} \frac{dT_e}{dt} = 319.6 D^2 \frac{(T_e - T_g)}{T_e^{1.5} T_g} \frac{1}{N} 4B^2 \left[\frac{1}{2\xi^2} \int_0^{\infty} dx \ln(\delta x) e^{-(\varepsilon + \xi)x^2} + \frac{1}{4\xi^2} \int_0^{\infty} dx e^{-(\varepsilon + \xi)x^2} - \frac{1}{4\xi^2} \int_0^{\infty} dx (1 - \xi x^2) E_i(-\xi x^2) e^{-\varepsilon x^2} \right], \quad (17)$$

where

$$E_i(-z) = - \int_z^{\infty} \frac{e^{-t}}{t} dt. \quad (18)$$

As always $\varepsilon + \xi > 0$, the first and second terms in the square brackets can be integrated without difficulty, while the last term becomes

$$- \frac{1}{4\xi^2} \left(1 - \frac{\xi}{2\varepsilon} \right) \int_0^{\infty} dx e^{-\varepsilon x^2} E_i(-\xi x^2) + \frac{1}{4\varepsilon\xi} \int_0^{\infty} dx e^{-(\varepsilon + \xi)x^2} \quad (19)$$

Two cases must be distinguished:

i) $\varepsilon > 0$ (prolate symmetric-top: $A > B$)

$$\int_0^{\infty} dx e^{-\varepsilon x^2} E_i(-\xi x^2) = - \sqrt{\frac{\pi}{\varepsilon}} \ln \left(\sqrt{\frac{\varepsilon}{\xi}} + \sqrt{1 + \frac{\varepsilon}{\xi}} \right), \quad (20)$$

ii) $\varepsilon < 0$ (oblate symmetric-top: $A < B$)

$$\int_0^{\infty} dx e^{-\varepsilon x^2} E_i(-\xi x^2) = -\sqrt{\frac{\pi}{|\varepsilon|}} \sin^{-1} \sqrt{\frac{|\varepsilon|}{\xi}}. \quad (21)$$

Hence we get for $\varepsilon > 0$

$$\begin{aligned} \frac{1}{n} \frac{dT_e}{dt} = & 319.6 D^2 \frac{(T_e - T_g)}{T_e^{1.5} T_g} \frac{1}{N} B^2 \frac{1}{\xi^2} \left[-\frac{1}{2} \left(\gamma + \ln \frac{4(\varepsilon + \xi)}{\delta^2} \right) \sqrt{\frac{\pi}{\varepsilon + \xi}} \right. \\ & \left. + \left(1 - \frac{\xi}{2\varepsilon} \right) \sqrt{\frac{\pi}{\varepsilon}} \ln \left(\sqrt{\frac{\varepsilon}{\xi}} + \sqrt{1 + \frac{\varepsilon}{\xi}} \right) + \left(1 + \frac{\xi}{\varepsilon} \right) \frac{1}{2} \sqrt{\frac{\pi}{\varepsilon + \xi}} \right], \quad (22) \end{aligned}$$

while for $\varepsilon < 0$, the factor $\sqrt{\pi/\varepsilon} \ln(\sqrt{\varepsilon/\xi} + \sqrt{1 + \varepsilon/\xi})$ in this formula has to be replaced by $\sqrt{\pi/|\varepsilon|} \sin^{-1} \sqrt{|\varepsilon|/\xi}$.

The last quantity to be evaluated is N in (5). Following the same procedures as before, we obtain

$$\begin{aligned} N = & \sum_{J=0}^{\infty} \sum_{K=0}^J (2J+1) e^{-\beta[BK(J+1) + (A-B)K^2]/T_g} \\ = & \int_0^{\infty} 2y dy \int_0^y dx e^{-(\xi y^2 + \varepsilon x^2)} = \frac{1}{2\xi} \sqrt{\frac{\pi}{\varepsilon + \xi}}. \quad (23) \end{aligned}$$

When we combine (22) and (23) and return δ , ε , and ξ back to the original quantities according to (15), we finally obtain the general expression for the cooling rate due to the rotational transitions in the symmetric-top molecules.

$$\begin{aligned} \left(\frac{1}{n} \frac{dT_e}{dt} \right)_{\text{rot(symm. top)}} = & -0.0275 D^2 B \frac{(T_e - T_g)}{T_e^{1.5}} \\ & \times \left\{ \ln \left(\frac{4A}{\beta B^2} \frac{T_e^2}{T_g} \right) - \frac{A}{A-B} - \gamma + \ln 4 - \left(1 - \frac{B}{2(A-B)} \right) \sqrt{\frac{A}{|A-B|}} 2g \right\}, \quad (24) \end{aligned}$$

($^{\circ}\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}$)

where

$$g = \begin{cases} \ln(\sqrt{(A-B)/B} + \sqrt{A/B}), & A > B \\ \sin^{-1} \sqrt{(B-A)/B}, & A < B. \end{cases}$$

For convenience, the relevant notations are summarized:

$$\beta = 1.16049 \times 10^4$$

A, B are the rotational constants in eV

D is the dipole moment in debye

T_e, T_g are the electron and gas temperatures in Kelvin.

This expression reduces to the case of the diatomic polar molecules in the limit of $A \rightarrow \infty$. That is, we readily obtain the following result:

$$\begin{aligned} \left(\frac{1}{n} \frac{dT_e}{dt} \right)_{\text{rot(diatom)}} = & -0.0275 D^2 B \frac{(T_e - T_g)}{T_e^{1.5}} \\ & \times \left\{ \ln \left(\frac{1}{\beta B} \frac{T_e^2}{T_g} \right) + \ln 4 - (1 + \gamma) \right\}. \quad (25) \end{aligned}$$

($^{\circ}\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}$)

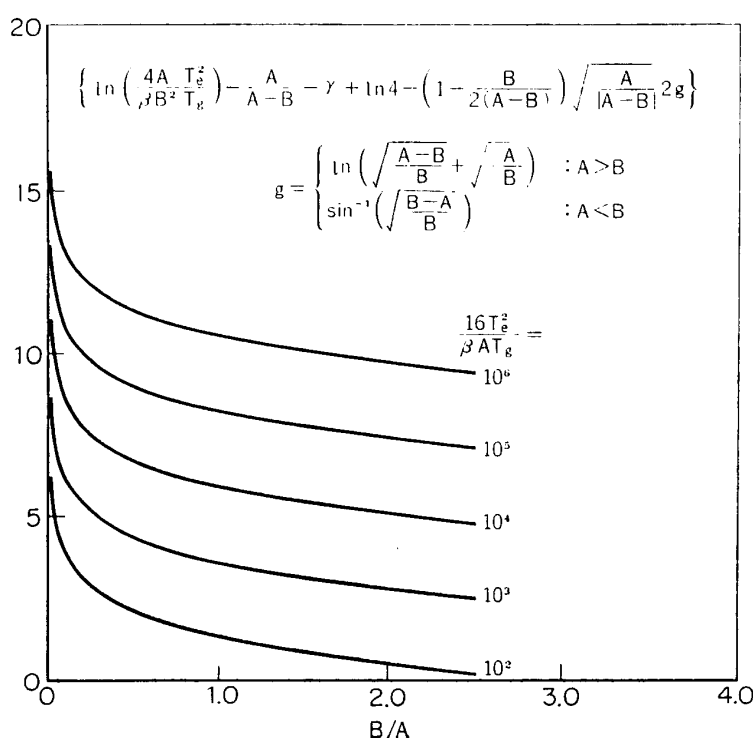


FIG. 1. The behavior of the curly brackets in eq. (24) as a function of B/A for the several values of the parameter $16T_e^2/\beta A T_g$.

The behavior of the curly brackets in (24) is shown as a function of B/A in Fig. 1 for the fixed parameter, $16T_e^2/(\beta A T_g)$. From these curves we see that the factor is slowly varying within a realistic range of these variables.

2.2 Rotational excitation of asymmetric-top molecules

We now briefly discuss a more general case, i.e., an asymmetric-top molecule. We shall confine ourselves to the case where the dipole moment is directed along one of the principle axes of inertia as in H_2O . In the expression (24) for the symmetric-top molecules, the rotational constant A is related to the moment of inertia around the axis parallel to the dipole moment. (At the same time the direction of the dipole moment was always a two-fold axis of symmetry.)

So it would be not unnatural to think that A and B in the expression (24) correspond respectively to a rotational constant associated with the principal axis parallel to the dipole moment (we call it F) and to a certain kind of average of the remaining two constants (say, G and H) in the asymmetric-top molecules.

As long as we take only the dipole interaction into account, G and H should appear symmetrically in the formula to be derived. Since the component of rotation around a dipole axis in the asymmetric-top molecule is not prohibited completely we could expect that a correction is needed to our quasi-symmetric-top model. But except for the molecules whose three

rotational constants are extremely different with each other, sample calculations (§ 3.1) show that such a correction is rather small for practical purposes.

We have tried the following typical symmetric operations M_r to (24) and compared the results with numerically calculated cooling rates for various sets of F , G and H :

Define $M_r = (1/2 \sum_{\nu=1,2} a_\nu^r)^{1/r}$, for $r=0$, we use $M_0 = \lim_{r \rightarrow 0} M_r = (\prod_{\nu=1,2} a_\nu)^{1/2}$, i.e., geometric mean. (a_1, a_2 are G and H in our case)

Then symmetric averages M_r are monotonously increasing function of r in the range $[-\infty, \infty]$.

It has been found that the geometric mean \sqrt{GH} of G and H has best approximated the numerical result in all cases. (e.g., in H_2O , the relative error is about less than 4%.)

After all we may write the rotational cooling rate for the general polar molecules approximately as follows

$$\begin{aligned} \frac{1}{n} \frac{dT_e}{dt} = & -0.0275 D^2 \sqrt{GH} (T_e - T_g) / T_e^{1.5} \\ & \times \left\{ \ln \left(\frac{4F}{\beta GH} \frac{T_e^2}{T_g} \right) - \frac{F}{F - \sqrt{GH}} - \gamma + \ln 4 - \left(1 - \frac{\sqrt{GH}}{2(F - \sqrt{GH})} \right) \right. \\ & \left. \times \sqrt{\frac{F}{|F - \sqrt{GH}|}} 2g \right\}, \quad (^\circ\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}) \end{aligned} \quad (26)$$

where

$$g = \begin{cases} \ln \left(\sqrt{\frac{F - \sqrt{GH}}{\sqrt{GH}}} + \sqrt{\frac{F}{\sqrt{GH}}} \right), & GH < F^2 \\ \sin^{-1} \sqrt{\frac{\sqrt{GH} - F}{\sqrt{GH}}}, & GH > F^2. \end{cases}$$

For user's convenience the quantities involved in this formula are summarized:

- F , rotational constant parallel to the dipole moment (eV)
- G, H , other two constants (eV)
- D , dipole moment (debye).

2.3 Vibrational excitations

The Born cross section for the vibrational transition through the dipole interaction is given by Takayanagi[14], as follows

$$\sigma(v \rightarrow v') = \frac{8\pi}{3k^2} (v' | D | v)^2 \ln \left| \frac{k+k'}{k-k'} \right|. \quad (27)$$

Following almost the same procedures as in the rotational transitions, we obtain

$$\begin{aligned} \frac{1}{n} \frac{dT_e}{dt} = & -319.6 \frac{1}{T_e^{1.5}} \sum_{\nu=0}^{\infty} \Delta E_{\nu \rightarrow \nu+1} [(v+1 | D | \nu)^2 n_\nu \cdot S_1 \\ & - (v | D | \nu+1)^2 n_{\nu+1} \cdot S_2], \quad (^\circ\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}) \end{aligned} \quad (28)$$

where $(v+1|D|v)$ is the v to $v+1$ transition dipole matrix element in debye, n_v is the normalized number of molecules in the v -th vibrational level, $\sum_v n_v = 1$, and S_1, S_2 are the two integrals over E in (7). If the gas temperature is not too high, molecules are populated mainly among the lower vibrational levels, so that the energy level is written as $E_v = \omega_e(v+1/2)$, $v = 0, 1, 2, \dots$, where ω_e is the fundamental vibrational energy. The level spacing Δ is constant and is equal to ω_e .

Using the relation $n_{v+1}/n_v = \exp\{-\beta\omega_e/T_g\}$, where ω_e is measured in eV,

$$\frac{1}{n} \frac{dT_e}{dt} = -319.6 \frac{\omega_e}{T_e^{0.5}} \frac{1}{\beta} K_0(\beta\omega_e/2T_e) e^{-\beta\omega_e/2T_e} \times [1 - e^{-\beta\omega_e(1/T_g - 1/T_e)}] \sum_{v=0}^{\infty} (v+1|D|v)^2 n_v. \quad (^\circ\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}) \quad (29)$$

Introducing a variable $x = \beta\omega_e/2T_e$, the rate is expressed as

$$\left(\frac{1}{n} \frac{dT_e}{dt}\right)_{\text{vib}} = -4.75 \times 10^{-6} \sqrt{T_e} [x e^{-x} K_0(x)] \times [1 - e^{-2x(T_e/T_g - 1)}] \sum_{v=0}^{\infty} (v+1|D|v)^2 n_v. \quad (^\circ\text{K} \cdot \text{cm}^3 \cdot \text{sec}^{-1}) \quad (30)$$

The above derivation suggests that the relation (30) can be applied also to the optically allowed electronic transition, provided that the cross section is mainly determined by the dipole interaction. (Then, ω_e and $\sum_v (v+1|D|v)^2 n_v$ have to be replaced by the threshold energy and the square of the transition dipole moment of the process.)

3. THE COOLING RATE OF THE ELECTRON GAS IN THE ENVIRONMENT OF COMETS

We now discuss the electron energy-loss rate for some molecules abundant in the cometary atmosphere. Water vapor and its dissociation products play a dominant role, and also carbon compounds may have non negligible effects.

We calculate in this section the cooling rates due to H_2O , OH , CO , CH , NH , NH_3 , H_2 and O . The first six molecules have large dipole moments and their rotational effects and vibrational effects are taken into account. For H_2 , rotational transitions by the quadrupole interaction, and for O , the fine structure transitions are considered. Direct numerical computations, without using the approximate formulae given in the previous sections, are carried out for all these molecules. The experimental or theoretical cross section data other than the Born results are used as far as possible. This is particularly so for the vibrational processes of some molecules, but as to the rotation we are compelled to use the Born cross section after all.

After we have performed numerical calculations using the Born cross section, the results have been in each case checked by the preceding analytical

TABLE I

Molecule	Rotational constant (eV) and vibrational fundamental energy (eV)	Dipole moment (debye)	Statistical weight g other than $2J+1$	Interaction	Method	Reference
H ₂ O	[*] $A=3.458^{-3}$ [27.877] $B=1.799^{-3}$ [14.512] $C=1.151^{-3}$ [9.285]	$D=1.85$	$g=1$ for a symmetric state on C_2 rotation around the 2-fold axis of symmetry. $g=3$ for an asymmetric state.	dipole	Born	Itikawa[8]
	(000) \rightarrow (010) 0.198 [1597] \rightarrow (100) + (001) 0.46 [3710] mean \rightarrow (011) 0.661 [5331] \rightarrow (101) 0.899 [7250] \rightarrow (111) 1.092 [8806]			dipole and quadrupole	Born	Itikawa[9]
	vib $B_0=2.297^{-3}$ [18.52] $D_0=2.23^{-7}$ [1.8 ⁻³] $L-S$ coupling const = -0.0173 [-139.8]		$D=1.66$	dipole	Born	Itikawa[7]
OH ($X^2\Pi$)	$\omega_e=0.463$ [3735] $\omega_e x_e=0.0103$ [82.8]	$(1 D 0)=0.031$ $(2 D 1)=0.039$		dipole	Born	Takayanagi[14]
CO ($X^1\Sigma^+$)	rot $B_0=2.384^{-4}$ [1.923] $D_0=8.00^{-10}$ [6.45 ⁻⁶]	$D=0.112$		dipole	Born	Takayanagi[14]
	vib $\omega_e=0.269$ [2170] $\omega_e x_e=1.669^{-3}$ [13.46] $B_0=7.357^{-3}$ [59.33] $D_0=5.70^{-6}$ [4.60 ⁻²]	$(1 D 0)=0.104$		dipole short range force quadrupole	Born experiment	Shulz[13]
H ₂ ($X^1\Sigma_g^+$)	rot $A=7.824^{-4}$ [6.31] $B=1.233^{-3}$ [9.94]	$Q=0.484$ (eas ²)	$g=3$ for odd J $g=1$ for even J	quadrupole (exchange and polarization) + dipole	Born closed coupling	Gerjouy Stein[3] Henry Lane[4]
NH ₃	rot $B_0=1.793^{-3}$ [14.46] $D_0=1.779^{-7}$ [14.35 ⁻⁴] $L-S$ coupling const = 0.00347 [27.95] $B_0=2.025^{-3}$ [16.33] $D_0=2.071^{-7}$ [16.7 ⁻⁴]	$D=1.468$	$g(K=3n)/g(K\neq 3n)=2$ and $g(K\neq 0)/g(K=0)=2$	dipole	Born	Itikawa[7]
CH ($X^2\Pi$)	rot $B_0=1.793^{-3}$ [14.46] $D_0=1.779^{-7}$ [14.35 ⁻⁴] $L-S$ coupling const = 0.00347 [27.95]	$D=1.46$			Born	Itikawa[7]
NH ($X^3\Sigma^-$)	rot $B_0=2.025^{-3}$ [16.33] $D_0=2.071^{-7}$ [16.7 ⁻⁴]	$D=2.17$			Born	Takayanagi[14]
O (3P_J) fine str	$E(J=2)=0$ $E(J=1)=0.01965$ [158.5] $E(J=0)=0.02808$ [226.5]		$g_{J=2}=5$ $g_{J=1}=3$ $g_{J=0}=1$	exchange	closed coupling	Breig Lin[2]

^{*} It is read, $A=3.458 \times 10^{-3}$ eV = 27.877 cm⁻¹
Molecular parameters are taken from Herzberg[5] and Nelson *et al.*[11]

formulae, and the accuracy of the analytical expressions (24), (26) and (30) has been evaluated.

3.1 Rotational transitions

H₂O

For the asymmetric molecule it can hardly be hoped that the energy loss rate will be represented in a closed form, because the energy levels and the wave functions of the asymmetric rotor are only determined by solving numerically the eigenvalue problem and there are no such simple expressions of the energy levels and transition matrix elements as for the symmetric-top molecule.

The rotational transition cross section of the asymmetric rotor due to dipole interaction is given in the Born approximation as follows[8]

$$\sigma(J\tau \rightarrow J'\tau') = \frac{8\pi}{3k^2} (2J'+1) D^2 \langle J'\tau' | J\tau \rangle_{110}^2 \ln \left| \frac{k+k'}{k-k'} \right|, \quad (31)$$

where

$$\begin{aligned} \langle J'\tau' | J\tau \rangle_{lm\delta} &= \sum_{K \geq 0} a_{\tau'K\nu'} a_{\tau K\nu} (-1)^K \begin{pmatrix} J & J' & l \\ K & -K & 0 \end{pmatrix}; \quad m=0 \\ &= a_{\tau'm\nu'} a_{\tau 00} (-1)^{m+\delta} \begin{pmatrix} J & J' & l \\ 0 & -m & m \end{pmatrix} + a_{\tau'00} a_{\tau m\nu} \begin{pmatrix} J & J' & l \\ m & 0 & -m \end{pmatrix} \\ &\quad + \sum_{K > m} a_{\tau',K-m,\nu'} a_{\tau K\nu} (-1)^{K-m} \frac{1}{\sqrt{2}} \begin{pmatrix} J & J' & l \\ K & m-K & -m \end{pmatrix} \\ &\quad + \sum_{K > 0} a_{\tau',K+m,\nu'} a_{\tau K\nu} (-1)^{m+K+\delta} \frac{1}{\sqrt{2}} \begin{pmatrix} J & J' & l \\ K & -m-K & m \end{pmatrix} \\ &\quad + \sum_{m > K > 0} a_{\tau',m-K,\nu'} a_{\tau K\nu} (-1)^{m-K+\nu'} \frac{1}{\sqrt{2}} \begin{pmatrix} J & J' & l \\ K & m-K & -m \end{pmatrix}; \\ &\hspace{15em} m > 0, \quad (32) \end{aligned}$$

and the quantities with and without prime respectively correspond to initial and final ones. Furthermore, the quantities in the above formula have the following meaning:

J is the total angular momentum; τ designates $2J+1$ sublevels for a given J ($\tau = -J, \dots, J$) (quantum number K for an asymmetric molecule is no longer a good quantum number and the degeneracy for $K \neq 0$ is removed; $a_{\tau K\nu}$'s are the coefficients of expansion of the asymmetric rotor function in terms of the symmetrized basis function linearly constructed from the symmetric-top molecule wave functions (Wang's functions) under the fixed J ; $\begin{pmatrix} J & J' & l \\ K & -K & 0 \end{pmatrix}$ is the $3j$ symbol; D is the dipole moment of the molecule which is parallel to the principal axis of the intermediate moment of inertia in H₂O (this is the reason why $\langle \dots \rangle_{110}$ appears in (31)); k' is the electron's final wave number after transition ($J, \tau \rightarrow J', \tau'$).

$a_{\tau K\nu}$ and the energy levels are simultaneously determined by solving the relevant secular equations as eigenvectors and eigenvalues. It is too lengthy to be shown here in details. (Concrete expression of the matrix to be solved is seen, *e.g.*, in the reference [8].)

The coefficient $\langle J'\tau'|J\tau\rangle_{110}$ and the energy levels $E_{J\tau}$ have been calculated up to $J=17$ and the integration in (2) where τ replaces K has been carried out. At the rotational temperature below about 1000°K under investigation, the adopted range of J may appear unnecessarily large. However, the energy spread of sublevels for a given J increases rapidly with J . For example, the energy level ($J=17, \tau=-17$) is lower than that of ($J=11, \tau=11$), so that we need the information of the state ($J=17, \tau=-17$) though ($J=17, \tau=17$) is not required. Thus the eigenvalue problem must be solved to a considerably high J . A similar situation is also found in other cases simpler than the water molecule. The accuracy of the rate is often sensitive to the highest state considered.

The resulting cooling rate is shown in Fig. 2 and tabulated in Table 2. We can understand that the water vapor is very competent to cool the electron gas if we pay attention to its abundance in comets. We have noticed in § 2.1 that the cooling rate is proportional to the square of the dipole moment and also to the rotational constant apart from the slowly varying logarithmic factor. Thus, strongly polar molecules with small atomic

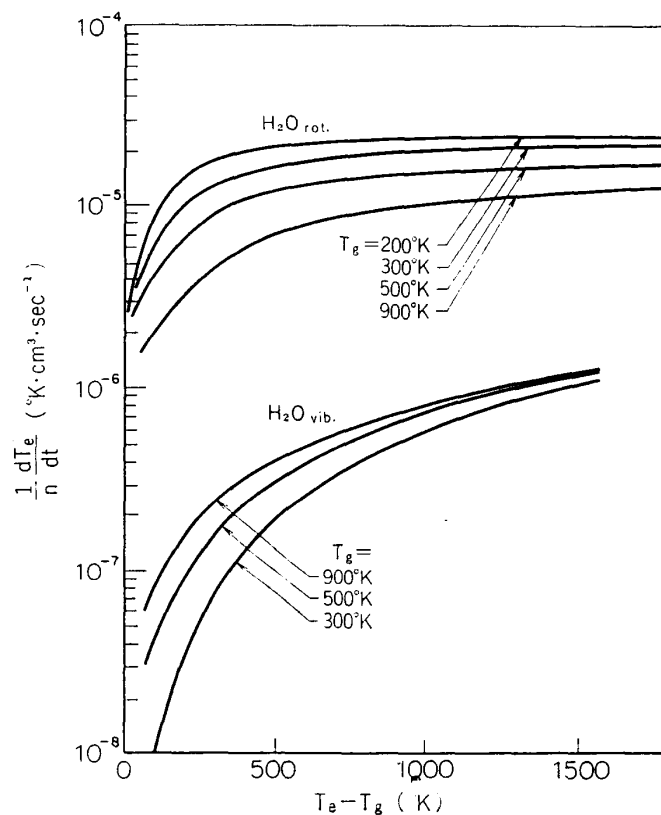


FIG. 2. The electron cooling rates for the rotational and the vibrational excitations of H_2O .

TABLE 2 $\frac{1}{n} dT_e/dt$ for H₂O rotation (°K cm³sec⁻¹)

$T_e \backslash T_g$	300	500	700	1000	1500	2000	3000
200	*8.75(-6)	1.70(-5)	2.05(-5)	2.27(-5)	2.36(-5)	2.35(-5)	2.26(-5)
300	—	1.01(-5)	1.49(-5)	1.82(-5)	2.02(-5)	2.07(-5)	2.05(-5)
500	—	—	6.51(-6)	1.16(-5)	1.52(-5)	1.67(-5)	1.75(-5)
700	—	—	—	6.33(-6)	1.12(-5)	1.40(-5)	1.50(-5)
900	—	—	—	1.97(-6)	7.81(-6)	1.06(-5)	1.29(-5)
1100	—	—	—	—	4.86(-6)	8.09(-6)	1.09(-5)

* 8.75(-6) = 8.75 × 10⁻⁶

masses are always good cooling agents.

NH₃

The molecule NH₃ is not necessarily significant for the electron gas cooling in the comets. We have calculated the cooling rate for this typical symmetric-top molecule so as to test the preceding expression (24) and also to apply it to the other fields of astrophysics. The statistical factor other than (2J+1) for NH₃ is shown in Table 1. When these factors are ignored, values calculated from (24) coincides with the direct numerical results within an error of 1%. The agreement is still very good when the statistical factor is taken into consideration. The maximum error then is below 1.5% over the whole temperature range calculated. (see Fig. 3)

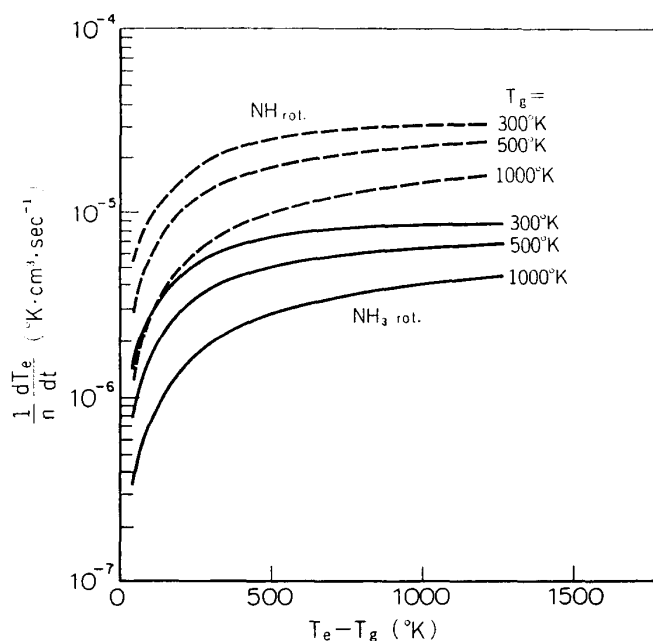


FIG. 3. The electron cooling rates for the rotational excitations of NH and NH₃.

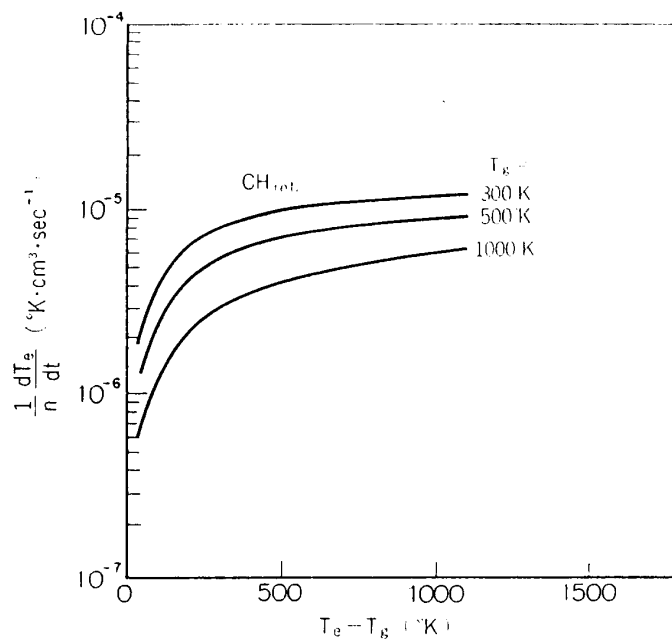


FIG. 4. The electron cooling rates for the rotational excitations of CH.

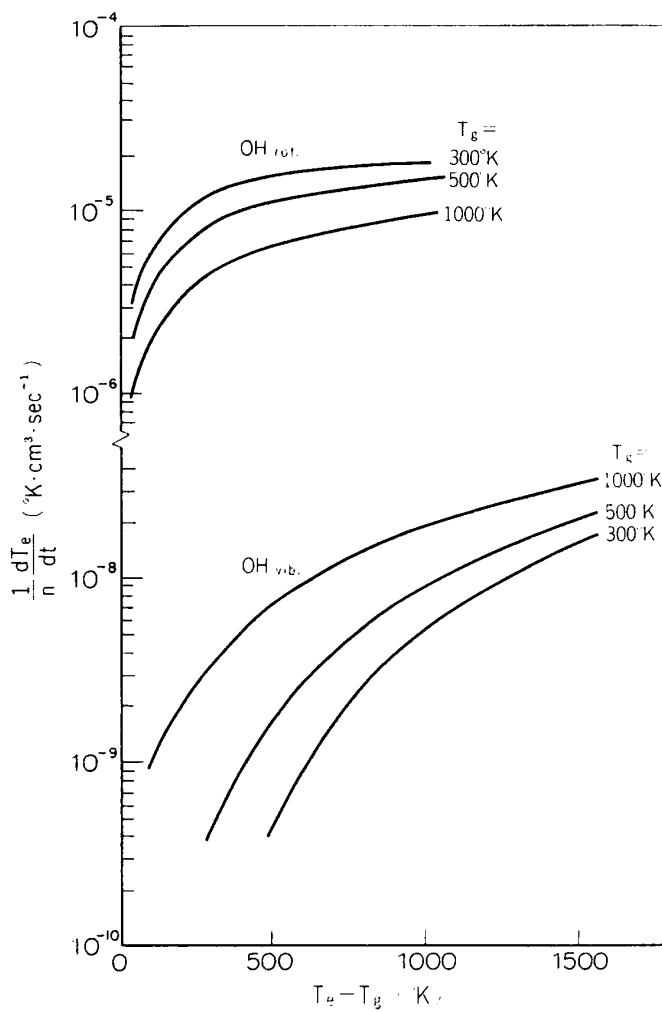


FIG. 5. The electron cooling rates for the rotational and the vibrational excitations of OH.

CH and OH

The ground states of these molecules are characterized by ${}^2\Pi$. Due to the spin-orbit interaction in CH, the molecule has a double sequence, where the lowest level of the sequence $\Pi_{1/2}, \Pi_{3/2}, \dots$ is lower than that of the other sequence $\Pi_{3/2}, \Pi_{5/2}, \dots$, while in OH the double sequence is an inverted one (the lowest of $\Pi_{3/2}, \Pi_{5/2}, \dots$ is lower than that of $\Pi_{1/2}, \Pi_{3/2}, \dots$). If the spin exchange effect is ignored, the transitions occur only within each sequence. Then we can utilize (3) as the cross sections for the dipole transitions, where for the two sequences for CH, for instance, $K=3/2$ and $1/2$. As is expected from their large dipole moments and small masses, the rate of cooling by these molecules are very large as shown in Figs. 4 and 5.

NH

The rotational sequence of NH is split into a triplet because of the spin-spin interaction. But the interaction is very weak in magnitude (see Table 1), so that the splitting is hardly necessary to be taken into account explicitly. So, we have handled the molecule as if it is in a ${}^1\Sigma$ state in the calculation. The molecule NH, which is believed to exist in the cometary atmosphere to a considerable amount, is most efficient to cool an electron gas among the candidates studied here. The result of calculations for this molecule is shown in Fig. 3.

CO

The molecule CO appears in the various astrophysical problems. As the ground state of CO is ${}^1\Sigma$, the treatment is simplest. The result is shown in Fig. 6. The rotational effect is very weak owing to the smallness of the dipole moment (0.112 debye) and of the rotational constant (1.92cm^{-1}). This molecule is extraordinary among the molecules of the astrophysical interest in the sense that the rate of cooling by the rotational transitions is far less than the one by the vibrational transitions over a wide range of electron temperature.

H₂

Hydrogen is not a polar gas. But because of its importance in astrophysics, we shall study the electron gas cooling by the rotational excitation of this molecule. The ground state of H₂ is a ${}^1\Sigma_g$ state just as in the case of CO. Since the molecule has no dipole moment, the quadrupole interaction must be invoked. The cooling rate has been calculated using the Born cross section given by Gerjuoy and Stein[3]. Mentzoni and Row's expression which was successful in the cases of N₂ and O₂ cannot be applied for the present purposes because of the larger level spacings in H₂. At present there is no analytical expression useful to this molecule. Some calculations of the rotational excitation have been done also in this case taking into account the effects (such as polarization, exchange) other than the point-multipole interaction. We see in Fig. 7 the result of calculations where Henry and Lane[4]'s cross sections are used for the transitions $J=0$ to 2 and $J=1$ to 3.

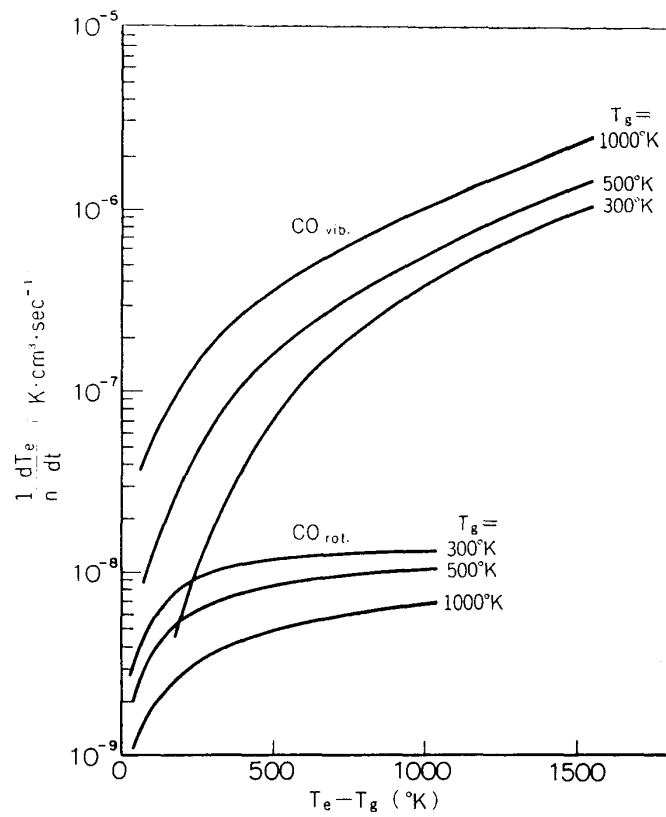


FIG. 6. The electron cooling rates for the rotational and the vibrational excitations of CO.

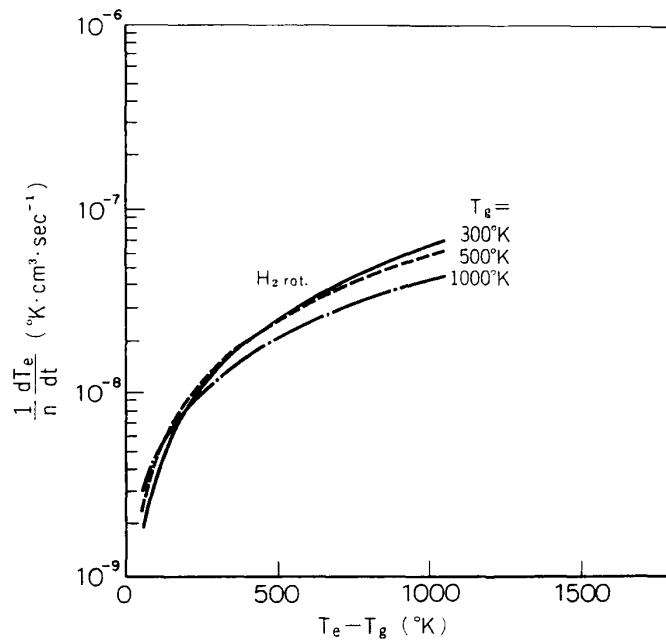


FIG. 7. The electron cooling rates for the rotational excitations of H₂.

3.2 Vibrational transitions

The vibrational cross section is sometimes very different from the Born cross section and there are not a few molecules which show resonant structures. So, we had better adopt an experimental or a refined theoretical cross sections as far as possible. However, no reliable values are available in most cases. For radicals, it is more difficult to obtain even a transition matrix element. Therefore, we have confined ourselves to the cases of H₂O, OH and CO.

H₂O

Water has three normal vibration modes: symmetric stretching, bending and asymmetric stretching, whose quanta are denoted ν_1 , ν_2 , ν_3 , respectively. Five transitions from the ground state are taken into account: (010), (100) + (001), (011), (101), (111). They give the greater part of contributions. For the cross sections of the first two transitions, data are taken from the calculations by Itikawa [9] and for the remaining processes semi-empirical formula are used with parameters given by Olivero *et al.* [12]. The inverse processes, if necessary, are included by the detailed balance relations. We can see not a little effect at high electron temperatures (Fig. 2).

OH

The transition dipole moments for hydroxyl are taken from the experimental values by d'Incan *et al.* [6], 0.031 and 0.039 debye for 0→1 and 1→2 transitions respectively. The results are shown in Fig. 5.

Owing to rather small transition dipole moments and considerable high threshold energies (0.443 eV for 0→1 transition) the cooling rate is very small naturally.

But the relative importance between a rotation and a vibration is strongly dependent on the individual molecule and we see a good example in next carbon monoxide as contrasted to OH.

CO

The dipole moment of CO is very small (0.112 debye) and the transition dipole moment for the vibration stands this value. The heaviness of the molecule in addition makes the rotational effect to be comparatively small.

To be more important, the CO vibration has huge resonant structures around 2 eV. Experimental data [13] has been used for the transitions from $\nu=0$ to 1, 2, 3 and 4.

We can thus understand the rapid increase of the rate toward the high electron temperature, in Fig. 6.

3.3 Fine structure level excitations

O

The electronic ground state of atomic oxygen is split into 3 sublevels with the small energy differences between each other. It is well known that the

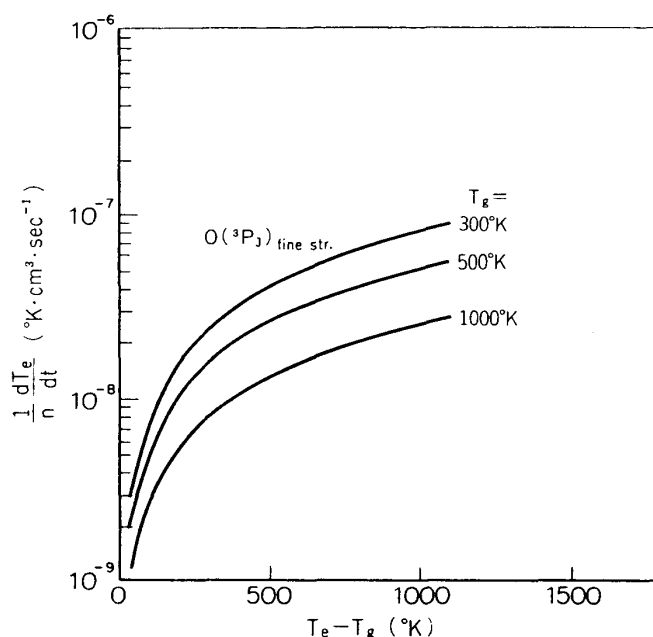


FIG. 8. The electron cooling rates for the fine structure level excitations of O.

transitions among them cause the electron gas to fair cooling in the upper atmosphere of the earth. Around the regions far apart from the comet, the atomic oxygen originated from the photodissociation of H_2O , OH and CO exists to a considerable amount.

The cross sections are taken from the theoretical calculation by Breig and Lin[2]. The result is shown in Fig. 8.

4. CONCLUSIONS

The atmospheres of comets are full of the polar molecules; evaporated parent molecules, chemical products and their dissociation products (mostly hydride radicals).

In these kinds of celestial objects, non-polar molecules, *e.g.*, N_2 , O_2 abundant in the terrestrial atmosphere, no more play a decisive role on the energetics of the electron gas.

We have calculated the electron cooling rate for the several polar molecules which are believed to exist in the cometary atmospheres.

The molecules H_2O , OH, CH, CO and NH are known to be the most efficient cooling agents for the electron gas there.

The analytical expressions of the cooling rates for the rotational and the vibrational processes have been constructed within the frame of the Born approximation (eqs. (24), (25) and (30)).

Also the extension to the general asymmetric-top molecules has been tried (eq. (26)). They have been confirmed to be accurate enough for the practical applications.

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