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Electron-impact excitation of molecular ions

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A simple expression is derived that relates the rate coefficient for dipole-allowed electron-impact excitation of a molecular ion in the Coulomb-Born approximation to the Einstein A coefficient for the corresponding radiative decay. Results are given for several molecular ions of astrophysical interest. A general analytic expression is obtained for the equilibrium rotational level populations in the ground vibrational state of any molecular ion excited by collisions with electrons. The expression depends only upon the electron temperature, the electron density, and the rotational constant of the molecular ion. A similar expression is obtained for neutral polar molecules.

I. INTRODUCTION

Theoretical treatments of molecular ion formation in the interstellar medium indicate that substantial abundances of diatomic molecular ions may be formed in the transition regions of planetary nebulas[1,2] and in the cooling gas behind a fast molecular shock.[3] Because these are regions where free electrons are present at temperatures of several thousand degrees and densities of 10^4-10^7 cm^{-3}, vibrational excitation of molecular ions in collisions with electrons may result in detectable infrared line emission. The detection of such radiation would provide a powerful diagnostic probe of conditions in the interstellar medium. Predictions of the emission intensity require values of the rate coefficients for electron-impact excitation of the vibrational levels.

We obtain here a simple expression relating the rate coefficient for dipole-allowed electron-impact excitation of a molecular ion in the Coulomb-Born approximation to the Einstein A coefficient for the corresponding radiative decay. We present values of the rate coefficient for vibrational excitation of several molecular ions of astrophysical interest for which Einstein A coefficients are available, and we discuss the radiative decay following vibrational excitation from a given rotational level of the ground vibrational state. We also investigate the rotational distribution in the ground vibrational state and we derive a general analytic expression for the level populations.

II. THE RATE COEFFICIENT FOR ELECTRON-IMPACT EXCITATION OF MOLECULAR IONS

In the Coulomb-Born approximation, the cross section for a dipole-allowed electron-impact excitation of a diatomic molecular ion is given by[4]

$$\sigma(vJ\rightarrow v'J') = \frac{2\pi}{3a_0^3\Delta E}|\langle v'J'|\mu|vJ\rangle|^2\frac{S(J,J')}{2J+1}\sigma_0(\Delta E,E)\ , \tag{1}$$

where $\langle v'J'|\mu|vJ\rangle$ is the dipole-matrix element for the transition; E is the energy of the incident electron, and ΔE is the energy of the transition; $S(J,J')$ is an angular factor; and $\sigma_0(\Delta E,E)$ is a function tabulated by Gailitis,[5] which is related to the free-free Gaunt factor g_{ff} by the expression

$$\sigma_0(\Delta E,E)=\frac{2\pi}{\sqrt{3}}\frac{\Delta E}{E}g_{ff}(\Delta E,E)a_0^2\ . \tag{2}$$

The Gaunt factor is given by Sommerfeld:[6]

$$g_{ff}=\pi\sqrt{3}\frac{\exp(2\pi\eta_i)}{[\exp(2\pi\eta_i)-1][\exp(2\pi\eta_f)-1]} \times x_0\frac{d}{dx_0}|F(-i\eta_i,-i\eta_f;1;x_0)|^2\ , \tag{3}$$

where $\eta_i=-(e^2/2a_0E)^{1/2}$, $\eta_f=-[e^2/2a_0(E-\Delta E)]^{1/2}$, $x_0=-4\eta_i\eta_f/(\eta_f-\eta_i)^2$, and F is the hypergeometric function.

The angular factors $S(J,J')$ for a diatomic molecular ion in a $^1\Sigma$ electronic state are given in terms of Wigner 3-j coefficients by the expression

$$S(J,J')=(2J+1)(2J'+1)\begin{pmatrix}J & 1 & J'\\ 0 & 0 & 0\end{pmatrix}^2\ . \tag{4}$$

For diatomic molecules represented by Hund's case (a)

$$S(J,J')=(2J+1)(2J'+1)\begin{pmatrix}J & 1 & J'\\ \Omega & 0 & \Omega'\end{pmatrix}^2\ , \tag{5}$$

where Ω is the projection quantum number of the total electronic angular momentum on to the nuclear axis. For a symmetric top molecule, Eq. (5) applies, with Ω replaced by the angular momentum K about the symmetry axis.[7] For Hund's case (b),

$$S(JN,J'N')=(2J+1)(2J'+1)(2N+1)(2N'+1) \times\begin{Bmatrix}N & 1 & N'\\ J' & S & J\end{Bmatrix}^2\begin{pmatrix}N & 1 & N'\\ \Lambda & 0 & \Lambda\end{pmatrix}^2\ , \tag{6}$$

where N is the nuclear rotational angular momentum quantum number, S is the spin quantum number, Λ is the projection quantum number of the electronic orbital angular momentum on the nuclear axis and $\{\ \}$ is a 6-j coefficient.

The angular factors for diatomic molecules are often called Hönl-London factors, here specialized to transitions within the same electronic state. They are symmetric in the primed and unprimed quantities and they satisfy the sum rules

$$\sum_J S(J,J')=2J'+1\ , \tag{7}$$

$$\sum_J \sum_N S(JN,J'N')=2J'+1\ . \tag{8}$$

Cases of intermediate coupling can be treated by standard procedures.[8-10]

Generalizing Eq. (1) and integrating σv over a Maxwellian velocity distribution we obtain for the rate coefficient for electron-impact excitation

$$\begin{aligned} q(vJ\rightarrow v'J') &= \langle \sigma v \rangle \\ &= \left[\frac{128\pi^3}{27mk_BT}\right]^{1/2} \frac{|\langle \alpha'|\mu|\alpha\rangle|^2}{a_0}\frac{S(\alpha,\alpha')}{2J+1} \\ &\quad \times G(\Delta E,T)\exp(-\Delta E/k_BT)\ , \end{aligned} \tag{9}$$

where α and α' are the sets of quantum numbers that specify the initial and final states, m is the electronic mass, k_B is Boltzmann's constant, T is the kinetic temperature of the exciting thermal electrons, and $G(\Delta E,T)$ is an average Gaunt factor, defined as

$$G(\Delta E,T)=\int_0^\infty g_{ff}(\Delta E,E=xk_BT+\Delta E)e^{-x}dx\ . \tag{10}$$

Values of $G(\Delta E,T)$ have been presented by Menzel and Pekeris,[11] Karzas and Latter,[12] Gayet,[13] Hummer,[14] and Carson.[15] Various approximate formulas exist.[16-18]

For $\Delta E \ll k_BT$ and $k_BT \ll e^2/a_0$, $G(\Delta E,T)$ is accurately represented by the classical expression[19]

$$G_c=\frac{\sqrt{3}}{\pi}\ln\left[\frac{4}{\exp(\gamma)}\left[\frac{2k_BTa_0}{\exp(\gamma)e^2}\right]^{1/2}\frac{k_BT}{\Delta E}\right]\ , \tag{11}$$

where γ is Euler's constant. For ΔE comparable to k_BT, expression (11) is not valid and G tends to a value near unity as k_BT tends to ΔE. We find that the numerical values for $k_BT \ll e^2/a_0$ can be reproduced to within 15% by

$$G(\Delta E,T)=G_c(\Delta E,T+T_0)\ , \tag{12}$$

where T_0 is such that $G_c(\Delta E,T_0)=1$.

Because matrix elements calculated for dipole-allowed vibrational transitions of molecular ions are often contained within Einstein A coefficients, it is useful to relate the collisional rate coefficients to them. The Einstein A coefficient for a dipole transition $(\alpha'\rightarrow\alpha)$ of frequency ν is given by

$$A(\alpha'\rightarrow\alpha)=\frac{64\pi^4\nu^3}{3hc^3}|\langle v'J'|\mu|vJ\rangle|^2\frac{S(\alpha,\alpha')}{2J+1}\ . \tag{13}$$

Eliminating the dipole moment from Eqs. (13) and (9), we obtain for the rate coefficient for electron-impact excitation of the transition $(vJ\rightarrow v'J')$

$$\begin{aligned} q(\alpha\rightarrow\alpha') &= A(\alpha'\rightarrow\alpha)\lambda^3\left[\frac{e^2}{k_BTa_0}\right]^{1/2}\frac{G(\Delta E,T)}{(24\pi^3)^{1/2}} \\ &\quad \times\frac{2J'+1}{2J+1}\exp(-\Delta E/k_BT)\ , \end{aligned} \tag{14}$$

where λ is the transition wavelength. The rate coefficient for the corresponding collisional deexcitation $(v'J'\rightarrow vJ)$ is given by

$$q(\alpha'\rightarrow\alpha)=A(\alpha'\rightarrow\alpha)\lambda^3\left[\frac{e^2}{k_BTa_0}\right]^{1/2}\frac{G(\Delta E,T)}{(24\pi^3)^{1/2}}\ . \tag{15}$$

If the radiative lifetimes of vibrationally excited states are independent of J', and if the energy spacing of the rotational states is much less than that between adjacent vibrational states, the normalization properties of the Hönl-London factors permit us to sum (14) and to obtain

$$\begin{aligned} q_{vv'} &= A_{v'v}\lambda^3\left[\frac{e^2}{k_BTa_0}\right]^{1/2}\frac{G(\Delta E,T)}{(24\pi^3)^{1/2}}\exp(-\Delta E/k_BT) \\ &= A_{v'v}\lambda^3\left[\frac{424K}{T}\right]^{1/2}G(\Delta E,T)\exp(-\Delta E/k_BT)\ , \end{aligned} \tag{16}$$

where $A_{v'v}=\sum_J A(v'J'\rightarrow vJ)$ and $q_{vv'}=\sum_{J'} q(vJ\rightarrow v'J')$.

In Table I we have compiled the Einstein A coefficients for $v=1\rightarrow 0$ radiative transitions of several molecular ions of astrophysical interest. We express the corresponding rate coefficients for electron-impact excitation

TABLE I. Rate coefficients for vibrational excitation of molecular ions by electron impact: $q=aT_4^{-1/2}\exp(-\Delta E/k_BT)$.

Ion	Electronic state	$A_{v=1\rightarrow 0}$ (s^{-1})	a ($cm^3\,s^{-1}$)	$\Delta E/k_B$ (K)	Reference
HeH^+	$X\,^1\Sigma^+$	1098	9.8×10^{-9}	4275	20
OH^+	$X\,^3\Sigma^+$	263	2.3×10^{-9}	4250	21
SH^+	$X\,^3\Sigma^-$	52	7.3×10^{-10}	3650	22
CH^+	$X\,^1\Sigma^+$	1.63	1.7×10^{-11}	3940	23
NO^+	$X\,^1\Sigma^+$	10.9	1.9×10^{-10}	3420	24,25
NH^+	$X\,^4\Sigma^+$	17	1.6×10^{-10}	4160	26,27

from $v=0$ to 1 in the form $q_{01}=aT_4^{-1/2}\exp(-\Delta E/k_BT)$, where $T_4=T/10\,000$ K. The average Gaunt factor has been taken as 1.1 throughout in calculating the parameter a. For a transition of energy difference $\Delta E/hc=3000$ cm^{-1}, the exact value of G varies only over the range 1.05–1.15 for $1000<T<10\,000$ K. The calculated Einstein A coefficients in Table I may be uncertain by about 20%.

III. RADIATIVE DECAY FOLLOWING VIBRATIONAL EXCITATION

Equation (16) shows that the rate of collisional deexcitation by electrons by means of any dipole transition is equal to the rate of spontaneous radiative decay when the electron density n_e equals a critical density $n_{\rm cr}$ defined by

$$n_{\rm cr}=\frac{A(\alpha'\rightarrow\alpha)}{q(\alpha'\rightarrow\alpha)}=\left[\frac{k_BTa_0}{e^2}\right]^{1/2}\frac{(24\pi^3)^{1/2}}{G(\Delta E,T)}\lambda^{-3}$$
$$=\left[\frac{T}{424k_B}\right]^{1/2}\frac{\lambda^{-3}}{G(\Delta E,T)}\ . \tag{17}$$

The critical density depends only on the wavelength of the transition and the temperature, and is independent of the dipole moment. Typical $v=1\rightarrow0$ vibrational transitions in molecular ions have wavelengths of 3–4 μm, corresponding to values of $n_{\rm cr}T_4^{-1/2}$ of order 10^{10} cm^{-3}. In astrophysical plasmas $n_eT_4^{-1/2}$ is often much less than 10^{10} cm^{-3}; in such cases electron impact deexcitation of vibrationally excited molecular ions may be neglected, and each collisional excitation from the $v=0$ to the $v=1$ state is followed by the emission of a $v=1\rightarrow0$ photon.

Consider the process in which a molecular ion in the state $\alpha=(0,J_1,N_1)$ is collisionally excited to the state $(1,J_2,N_2)$ and then decays radiatively to $(0,J_3,N_3)$. The rate r at which such a process occurs is given by

$$r=q_{01}n_en_if(J_1,N_1)\gamma(J_1,N_1;J_2,N_2;J_3N_3)\ , \tag{18}$$

where n_i is the density of molecular ions, $f(J_1,N_1)$ is the fractional population in the $(v=0,J_1,N_1)$ state, and $\gamma(J_1,N_1;J_2,N_2;J_3N_3)$ is the fraction of vibrational excitations from $(v=0,J_1,N_1)$ which leads first to the $a(v=1,J_2,N_2)$ state, and which subsequently decays radiatively to $(v=0,J_3,N_3)$. If collisional deexcitation from the $(v=1)$ level is negligible, γ is related to the Hönl-London factors by

$$\gamma(J_1,N_1;J_2,N_2;J_3,N_3)=\frac{S(J_1,N_1,J_2,N_2)}{2J_1+1}\times\frac{S(J_2,N_2,J_3,N_3)}{2J_2+1}\ . \tag{19}$$

The total emissivity ϵ of photons in the $(v=1,J_2,N_2)\rightarrow(v=0,J_3,N_3)$ transition is given by the sum

$$\epsilon=q_{01}n_en_i\sum_{J_1,N_1}f(J_1,N_1)\gamma(J_1,N_1;J_2,N_2;J_3,N_3)\ , \tag{20}$$

from which the emission spectrum can be calculated once the rotational distribution in the ground vibrational state is known.

IV. ROTATIONAL DISTRIBUTION IN THE GROUND VIBRATIONAL STATE

We consider the rotational distribution in the ground vibrational state of a molecular ion for which dipole-allowed radiative and collisional processes dominate all others. We may neglect processes in which vibrational excitation followed by radiative decay changes the rotational quantum number because dipole matrix elements for vibrational excitation are usually one to two orders of magnitude smaller than those for pure rotational excitation. We include only collisional transitions induced by electron impact. We discuss first a $^1\Sigma$ electronic state.

With our assumptions, the equations of statistical equilibrium for the steady-state-level populations have the solution

$$f(J)=f(J-1)\left[1+\frac{n_{\rm cr}^J}{n_e}\right]^{-1}\frac{2J+1}{2J-1}\times\exp[-(E_J-E_{J-1})/k_BT]\ , \tag{21}$$

where $n_{\rm cr}^J$ is the critical density defined by Eq. (17) for the transition $(v=0,J\rightarrow v=0,J-1)$, and E_j is the energy of level j. Using Eqs. (11) and (17) we find that for a molecular ion of rotational constant B, the critical density for level J is given by

$$n_{\rm cr}^J=\left[\frac{T}{424k_B}\right]^{1/2}\frac{(2BJ)^3}{G(2BJ,T)}$$
$$=\frac{47.0T_4^{1/2}J^3B^3}{\ln[157T_4/(JB)^{2/3}+3.35]}\ , \tag{22}$$

where B is measured in cm^{-1} for the logarithmic term.

The fractional population in level J is, therefore,

$$f(J)=f(0)\prod_{J'=1}^{J}\left[\frac{2J'+1}{2J'-1}\exp(-2BJ'hc/k_BT)\left[1+\frac{47.0T_4^{1/2}(J')^3B^3}{n_e\ln(157T_4/(J'B)^{2/3}+3.35)}\right]^{-1}\right]\ . \tag{23}$$

If $(k_BT/hc)\gg BJ^2$, then the Boltzmann factors in (23) can be set equal to unity. Further, unless $f(J)$ is very small, J' can be replaced by J inside the logarithm with negligible loss of accuracy. With these approximations, $f(J)$ can be written as a function $F_J(x_J)$ of a single variable x_J, where

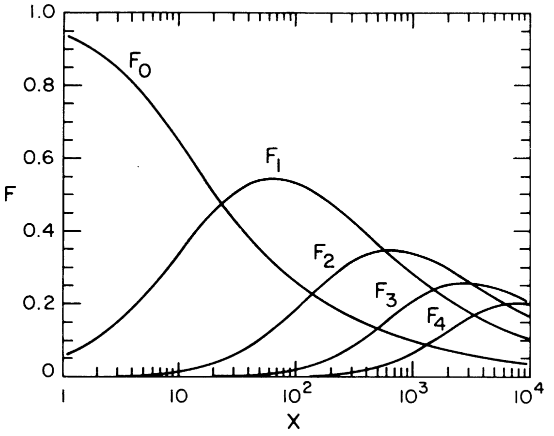

FIG. 1. Fractional population functions $F_J(x)$ (see text).

$$x_0 = x_1 \ ,$$

$$x_J = \frac{n_e T_4^{-1/2} \ln[157 T_4/(JB)^{2/3} + 3.35]}{B^3} \quad (J > 0) \ . \tag{24}$$

The functions $F_J(x)$ are plotted in Fig. 1 for $10 < x < 10^4$ and $J < 5$.

In cases where the rotational levels are split by coupling to a nonzero electron spin, the solution to the equations of statistical equilibrium derived above may be carried over, provided that the splitting parameter is much less than the rotational constant and that transitions with $|\Delta N| = 3$ have negligibly small dipole moments, as is the case when Hund's case (b) is applicable. Under these conditions, each level with a given rotational quantum number N has the same energy E_N and the same critical density n_{cr}^{N} for all possible transitions to levels $N-1$. The equations of statistical equilibrium require

$$f(J,N) = f(J',N-1) \left[1 + \frac{n_{\mathrm{cr}}^{N}}{n_e} \right]^{-1} \frac{2J+1}{2J'+1} \times \exp[-(E_N - E_{N-1})/k_B T)] \tag{25}$$

for all N, J, and J', implying that the fractional population in (J,N) is given by

$$f(J,N) \simeq \frac{(2J+1)}{(2N+1)(2S+1)} F_N(x_N) \ . \tag{26}$$

With a further extension of the above treatment, the function plotted in Fig. 1 may be used to obtain rotational distribution in the ground vibrational state of a *neutral* polar molecule under conditions where dipole-allowed electron-impact excitations dominate. Given the rate coefficient for electron-impact excitation obtained using a modified Born approximation by Dickinson and coworkers,[28,29] we find that when $k_B T/hc \gg BJ^2$, the fractional population of a neutral polar molecule in a level (J,N) is given by

$$f(J,N) \simeq \frac{(2J+1)}{(2N+1)(2S+1)} F_N(y_N) \ , \tag{27}$$

where

$$y_0 = y_1 \ ,$$

$$y_N = \frac{\frac{2}{3} n_e T_4^{-1/2} \ln(4394 \kappa T_4/NB + 2.25\kappa)}{B^3} \quad (N > 0) \ , \tag{28}$$

B in the logarithm is in cm^{-1}, and for a molecule of dipole moment D debyes,

$$\kappa = \begin{cases} 1 \quad (D \le 1.53) \\ \dfrac{2.13 \exp(-1.18/D^3)}{D} \quad (D \ge 1.53) \ . \end{cases} \tag{29}$$

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