

ROTATIONAL EXCITATION ($J = 0 \rightarrow J = 2$) OF POLAR MOLECULES IN THE SUDDEN APPROXIMATION

M.J. JAMIESON

*Department of Computing Science, University of Glasgow,
Glasgow, UK*

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The cross section for impact excitation of $J = 2$ rotational levels of polar molecules in the ground state is derived in an impact parameter formulation of the sudden approximation, assuming a dipole interaction. A simple expression for the rate coefficient is given and some results for excitation of CN by protons and electrons are presented.

1. Introduction

Excitation of rotational levels of polar molecules in the ground state by charged particle impact is of astrophysical interest in the interpretation of observations relevant to the cosmic black body background radiation [1]. Previous study includes close coupled wave calculations [2,3], modified Born calculations [4], use of the exponential approximation of Callaway and Bauer [2,5] and close coupled impact parameter calculations [6].

Close coupled calculations [3,6] show that at low energies the dipole-dipole sequence of transitions is the dominant mechanism for excitations involving multiple changes of rotational quantum number. An expression for the $J = 0$ to $J = 2$ cross section is derived below in which the interaction between the projectile and target is assumed to be only dipole. The sudden approximation [7] is used since the excitation energies are very small. An impact parameter formulation is employed. Thus there are two lower limits of energy for the validity of the method, being that below which the collision cannot be considered sudden and that below which the impact parameter method fails. The impact parameter method is not so good for excitation of $J = 2$ states by electrons as for that of $J = 1$ states [6]. At high energies the dominance of the dipole-dipole sequence cannot be assumed but results may be obtained from the Born approximation to the solution of the impact parameter equations for the quadrupole interaction [8].

2. Impact parameter formulation of the sudden approximation

A dipole potential is assumed.

$$V(r) = (qD/R^2)\hat{r} \cdot \hat{R}, \quad (1)$$

where q is the charge of the projectile of mass m travelling with speed v , energy E , relative to the target molecule, D is the dipole moment of the molecule, R is the position vector of the projectile relative to the centre of mass of the molecule and \hat{r} is the direction of the molecular axis. We strictly should modify the potential at short range but since most of the cross section comes from moderate to large impact parameters we consider this unnecessary. We assume that the projectile trajectory is a straight line at impact parameter ρ , and choose the axis of quantization of the molecule to be perpendicular to the plane containing the trajectory and the centre of mass of the molecule.

Then

$$\hat{r} \cdot \hat{R} = \sin \theta \cos(\Phi - \phi), \quad (2)$$

where $\hat{r} = (\theta, \phi)$, $\hat{R} = (\frac{1}{2}\pi, \Phi)$ the azimuthal angle being measured from the direction antiparallel to the trajectory, and

$$R^2 = \rho^2 + v^2 t^2. \quad (3)$$

In the sudden approximation [7], at impact parameter ρ , the probability for exciting the $|JM\rangle$ state from the ground state is

$$P_{JM}(\rho) = \left| \langle JM | \exp \left[-iqD\rho \sin\theta \sin\phi \int_{-\infty}^{\infty} R^{-2} \sin\Phi dt \right] | 00 \rangle \right|^2 = |\langle JM | \exp[-(2iqD/v\rho) \sin\theta \sin\phi] | 00 \rangle|^2. \quad (4)$$

Hence

$$P_{JM}(\rho) = P_{J-M}(\rho) = \frac{(2J+1)(J-M)!}{16(J+M)!\pi^2} \left| \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta P_J^M(\cos\theta) \exp[iM\phi + (2iqD/v\rho)\sin\theta \sin\phi] \right|^2. \quad (5)$$

This integral may be evaluated with the aid of properties of Bessel functions [9]. From equations (9.1.42) and (9.1.43) of ref. [9] we see that

$$\int_0^{2\pi} \exp(im\phi + iz \sin\phi) d\phi = 2\pi i^m J_m(z), \quad (6)$$

and so

$$P_{JM}(\rho) = P_{J-M}(\rho) = \frac{(2J+1)(J-M)!}{4(J+M)!\pi} \left| \int_0^\pi \sin\theta P_J^M(\cos\theta) J_M(2iqD \sin\theta/v\rho) d\theta \right|^2, \quad (7)$$

which is zero if $J-M$ is odd since the integrand then contains odd powers of $\cos\theta$; this is a consequence of the choice of quantization axis. Specializing to $J=2$ we have

$$P_{2\pm 2}(\rho) = \frac{15}{32\pi} \left| \int_0^\pi \sin^3\theta J_2(2iqD \sin\theta/v\rho) d\theta \right|^2, \quad (8)$$

$$P_{20}(\rho) = \frac{5}{16\pi} \left| \int_0^\pi \sin\theta (3 \cos^2\theta - 1) J_0(2iqD \sin\theta/v\rho) d\theta \right|^2. \quad (9)$$

From equation (11.4.10) of ref. [9] we see that

$$P_{2\pm 2}(\rho) = \frac{15}{8} j_2^2(2qD/v\rho), \quad (10)$$

$$P_{20}(\rho) = \frac{5}{4} [(3v\rho/2qD) j_1(2qD/v\rho) - j_0(2qD/v\rho)]^2 = \frac{5}{4} j_2^2(2qD/v\rho). \quad (11)$$

The total probability for populating the $J=2$ state is

$$P(\rho) = 5j_2^2(2qD/v\rho) \quad (12)$$

and the cross section is

$$Q(E) = 2\pi \int_0^\infty P(\rho) \rho d\rho = (20\pi m q^2 D^2/E) \int_0^\infty j_2^2(x) x^{-3} dx = \frac{5}{16} \pi m q^2 D^2/E, \quad (13)$$

from equations (11.4.33) and (15.1.20) of ref. [9].

The rate coefficient at temperature T , assuming maxwellian distribution of projectile speeds, is

$$\alpha(T) = (\pi m)^{-1/2} (2/kT)^{3/2} \int_{6Bhc}^{\infty} E \exp(-E/kT) Q(E) dE, \quad (14)$$

where $6Bhc$ is the excitation energy, B being the rotational constant.

$$\alpha(T) = \frac{5}{3} (2\pi m/kT)^{1/2} q^2 D^2 \exp(-6Bhc/kT). \quad (15)$$

3. Results

With E in eV, D in debye and B in cm^{-1} we obtain the following expressions for Q and α for excitation by electrons and protons respectively.

$$Q(E) = 1.03D^2 E^{-1} \times 10^{-16} \text{ cm}^2, \quad Q(E) = 1.89D^2 E^{-1} \times 10^{-13} \text{ cm}^2; \quad (16)$$

$$\alpha(T) = 7.42D^2 T^{-1/2} \exp(-8.63BT^{-1}) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}, \quad (17)$$

$$\alpha(T) = 3.18D^2 T^{-1/2} \exp(-8.63BT^{-1}) \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}.$$

We compare in table 1 cross sections for excitation of CN by protons and electrons with the results of close coupled impact parameter [6] and wave [3] calculations. The potential used in the latter was that of Crawford et al. [3], which included polarization and quadrupole parts, in which $D = 1.45$ debye and B was taken as 1.90 cm^{-1} . Exact agreement is not expected but the sudden approximation gives reasonable estimates over the energy ranges given. At very low energies the impact parameter method is not valid and the collision is not sudden; at high energies the quadrupole interaction, omitted here, becomes important.

For electron excitation at 1000 K the rate coefficient from eq. (17) is $4.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ compared with $2.3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ from the close coupling calculations of Allison and Dalgarno [3]. The poor agreement is because the rate coefficient at this temperature depends strongly on low energy cross sections for which eq. (17) is poor. Better agreement is expected at higher temperatures. At 10 000 K, the temperature of H II regions, the rate coefficients are $1.6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ for electron impact and $6.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for proton impact.

Table 1
Cross sections for excitation of CN by protons and electrons

Energy protons (eV)	Cross sections		Energy electrons (eV)	Cross sections	
	sudden (10^{-14} cm^2)	close coupled impact parameter [6] (10^{-14} cm^2)		sudden (10^{-16} cm^2)	close coupled wave [3] (10^{-16} cm^2)
0.4	99.3	84.4	0.05	43.3	21.2
1.0	39.7	55.8	0.1	21.6	12.1
25.0	1.59	1.86	0.2	10.8	7.1
50.0	0.79	0.92	0.4	5.4	4.4
100.0	0.40	0.46	0.6	3.6	3.5
500.0	0.08	0.09	0.8	2.7	3.0
			1.0	2.2	2.7

4. Conclusion

The sudden approximation yields reasonable results, simply, of cross sections for excitation of the rotational states of rigid rotator molecules by charged particle impact. For $|\Delta J| = 1$ transitions care must be taken because of the long range of the dipole interaction [6]. For $J = 0$ to $J = 2$ excitation through a dipole interaction the cross sections and rate coefficients are given by simple expressions. We note that care must be taken in extending the method to excitations involving large changes of quantum number since the energy differences become large. Very accurate and low energy cross sections require numerical solution of the appropriate close coupled equations.

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