J. Phys. B: At. Mol. Opt. Phys. **29** (1996) 1525–1530. Printed in the UK

Calculation of excitation cross sections for the lowest five dipole-allowed transitions in e–N_2 scattering

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Received 14 September 1995, in final form 26 January 1996

Abstract. Two methods have been used in the calculation of the integral excitation cross sections (ICSs) for the first time for the lowest five dipole-allowed transitions in e–N_2 scattering in the energy range from 200 to 1000 eV. The first method uses the universal extrapolation function together with the differential cross sections (DCSs) data, while the other uses Lassettre's equation and the Bethe theory. Good agreement has been obtained between the two methods at 500 eV. The calculation demonstrates that a significant contribution to the ICS comes from small scattering angles (0°–4.18°) where the experimental data are not available. Therefore a good extrapolation function is necessary in the calculation of the ICS from the DCS measurement in order to avoid the large uncertainties in the region of small scattering angles.

1. Introduction

The nitrogen molecule is the most abundant molecule in the Earth's atmosphere. Processes such as excitation, photoionization, photoexcitation, predissociation by solar radiation and electron impact play important roles in the Earth's energy balance. Although a great deal of effort has been devoted to understanding these processes, only a few publications have discussed the lowest five dipole-allowed transitions: $X\ ^1\Sigma_g^+ \rightarrow b\ ^1\Pi_u$, $X\ ^1\Sigma_g^+ \rightarrow b'\ ^1\Sigma_u^+$, $X\ ^1\Sigma_g^+ \rightarrow c\ ^1\Pi_u$, $X\ ^1\Sigma_g^+ \rightarrow c'\ ^1\Sigma_u^+$ and $X\ ^1\Sigma_g^+ \rightarrow o\ ^1\Pi_u$. Theoretically, molecular wavefunctions are more complicated than atomic ones. It is often difficult even to perform a calculation in the Born approximation. Experimentally, the vibrational states of the above transitions (17 for $b\ ^1\Pi_u$, 25 for $b'\ ^1\Sigma_u^+$, for example) overlap with each other so that the difficulty in the measurement is increased.

The absolute generalized oscillator strengths (GOSs) for e–N_2 scattering at 500 eV have been measured by Silverman and Lassettre (1965). Their 12.85 eV band (energy range 11.4–13.6 eV) and 13.99 eV band (energy range 13.6–15.0 eV) basically covered the lowest five dipole-allowed transitions. The GOSs of these bands are the sum of the individual GOSs of each vibrational state. Chung and Lin (1972), and Domenicucci and Miller (1977) calculated the GOSs and differential cross sections (DCSs) in a Born approximation using Hartree–Fock wavefunctions. Their results depend on the wavefunctions used in the calculations. Bielschowsky *et al* (1989) performed the same calculation but used configuration-interaction (CI) wavefunctions. In comparison with Lucas's (1984) measurement a better agreement was obtained than when Hartree–Fock wavefunctions were employed. However, the important integral excitation cross sections (ICSs) for these five dipole-allowed transitions have not been evaluated in the energy range 200 to 1000 eV.

0953-4075/96/081525+06$19.50

In this paper we have used the universal function (Msezane and Sakmar 1994) to extrapolate the GOSs for the lowest five dipole-allowed transitions to K^2 (momentum transfer squared) = 0, and the DCS data to evaluate the ICS at 500 eV. Lassettre's formula (Lassettre 1965) and Vriens's equation (Vriens 1967) have also been used to calculate the ICSs from 200 to 1000 eV. A good agreement between the two methods has been achieved at 500 eV. Both methods indicate the importance of the extrapolation function in the calculation of the ICS from DCS measurement.

2. Theory

Two methods have been used in the calculation of the ICSs for the lowest five dipole-allowed transitions in e–N_2 scattering. The first method uses the universal extrapolation function together with the DCSs data. The second method uses Lassettre's equation and the Bethe theory.

2.1. First method

The universal function, which can be used to extrapolate the GOSs to $K^2 = 0$ for the dipole-allowed transitions, was first introduced by Msezane and Sakmar (1994). It is particularly useful for the experimentalists to interpret and normalize their data (Msezane *et al* 1994). For the electron–molecule collision, it can be expressed (Chen and Msezane 1995) (atomic units are used throughout this paper unless otherwise indicated) as

$$f(K^2) = \sum_i f_i = \sum_i -f_i^{\mathrm{o}}\left[1 - \frac{2}{1 + K^2/2w_i}\right] \tag{1}$$

where $f(K^2)$ is the GOS for the transition to an electronic state with several vibrational states, f_i, f_i^{o} and w_i are, respectively, the GOS, the optical oscillator strength (OOS) and the excitation energy for each vibrational state. DCSs and GOSs are related through

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_i = f_i \frac{k_f}{k_i}\frac{2}{w_i K^2} \tag{2}$$

where $(\mathrm{d}\sigma/\mathrm{d}\Omega)_i$ is the DCS of the ith vibrational state, and k_i and k_f are the momenta of the electron before and after the collision. Substituting (1) and (2) into the formula $\int_0^{\theta_s}(\mathrm{d}\sigma/\mathrm{d}\Omega)\mathrm{d}\Omega$, we obtain (3), which can be used to evaluate the ICS of the transition to an electronic state contributed from the region of small scattering angles:

$$\begin{aligned}\int_0^{\theta_s}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\mathrm{d}\Omega &= \sum_i \int_0^{\theta_s}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_i \mathrm{d}\Omega \\ &= \sum_i \frac{\pi f_i^{\mathrm{o}}}{w_i E}\left[\ln\frac{2E - w_i - 2E\sqrt{1 - w_i/E}\cos\theta_s}{2E - w_i - 2E\sqrt{1 - w_i/E}}\right. \\ &\quad \left. -2\ln\frac{1 - \sqrt{1 - w_i/E}\cos\theta_s}{1 - \sqrt{1 - w_i/E}}\right]\end{aligned} \tag{3}$$

where θ_s is the smallest angle at which the measurement is available and E is the impact energy. The contribution to the ICS from θ_s to the maximum angle of the measurement can be obtained by using a spline curve to fit the DCS data and integrating the fitting equation. Finally, the ICS is the sum of the results of equation (3) and the integration of the spline. The resultant ICS using this method is for a given impact energy value.

2.2. Second method

In electron–atom and electron–molecule collisions, if the impact energy is high enough so that the Born approximation holds, GOS data can be fitted with a polynomial by the least-squares fitting process. The general form of the polynomial for the dipole-allowed transitions may be expressed as (Lassettre 1965):

$$f(K^2) = \frac{f_0}{(1+x)^6}\left[1 + f_1\left(\frac{x}{1+x}\right) + f_2\left(\frac{x}{1+x}\right)^2 \cdots\right] \tag{4}$$

where $x = K^2/\alpha^2$, $\alpha = \sqrt{2I} + \sqrt{2(I-w)}$ with I the ionization energy of the atom or molecule and w the transition energy. The ICSs can be obtained from the integral (Vriens 1967)

$$\sigma = \frac{\pi}{Ew}\int_{K_{\min}}^{K_{\max}} \frac{f(K^2)}{K^2}\mathrm{d}K^2 \tag{5}$$

where E is the impact energy. Substituting (4) into (5) we obtain:

$$\sigma = \frac{\pi}{Ew}[\ln(8cE) - \phi]f_0 \tag{6}$$

where c and ϕ are calculated from the equations

$$\ln c = 2\ln\left(\frac{\alpha}{2w}\right) - \frac{137}{60} + \frac{f_1}{6} + \frac{f_2}{42} + \frac{f_3}{168} + \frac{f_4}{504} + \frac{f_5}{1260}\cdots \tag{7}$$

and

$$\phi = \frac{w}{2E} + \frac{(f_1 - 6)w^2}{2\alpha^2 E} \tag{8}$$

with $f_0, f_1, f_2, f_3 \ldots$ being the coefficients of (4). This second method allows us to evaluate the ICSs at the high impact energies as long as the Born approximation is applicable.

3. Results

The OOSs and w_i used in the calculation using equation (1) of the first method were taken from Chan *et al* (1993). The total OOS of 43 vibrational states is 1.0256, which is equal to the sum of the OOSs of the 12.85 eV band and the 13.99 eV band. Figure 1 shows the results of (1) in which 43 vibrational states from the five dipole-allowed transitions are involved in the calculation. The full circles are the measurements by Lucas (1984); the broken curve shows the Born approximation using configuration-interaction wavefunctions (Bielschowsky *et al* 1989); the full curve is the result of equation (1) and the crosses are the data of Silverman and Lassettre (1965) which are equal to the sum of the GOSs of the 12.85 eV band and the 13.99 eV band of table 1. Their original data have been multiplied by a factor of 0.754 (Skerbele and Lassettre 1970) to correct for the streaming error in McLeod gauges. The overall agreement is good between $K^2 = 0$ and $K^2 = 1$ au. This demonstrates that a good extrapolation for the GOSs of the five dipole-allowed transitions can be obtained by using the universal function.

The results of equation (3) at 500 eV for each electronic state are given in table 2. After adding all the data in table 2, the ICS from the scattering angle $\theta = 0^\circ$ to $\theta = \theta_s = 4.18^\circ$ (the unmeasured angular range) is 3.028×10^{-17} cm^2 (4.18° is the smallest angle in the measurement of Silverman and Lassettre (1965)).

The contribution from θ_s to the maximum angle 13.5° in the measurement is obtained by using a spline curve to fit the data of columns 4 and 7 in table 1 and integrating the fitting

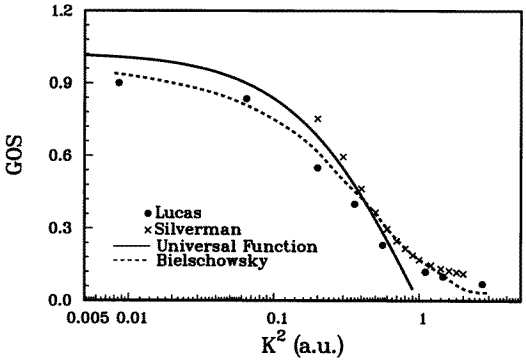

Figure 1. GOSs versus K^2 for the lowest five dipole-allowed transitions in e–N_2 scattering. The full circles are the measurements by Lucas (1984); the broken curve is the Born approximation using configuration-interaction wavefunctions (Bielschowsky *et al* 1989); the full curve is the result of equation (1) and the crosses are the data of Silverman and Lassettre (1965).

Table 1. GOSs and DCSs for the 12.85 eV and the 13.99 eV bands.

	12.85 eV band			13.99 eV band		
K^2	θ°	GOS (au)	DCS (au)	θ°	GOS (au)	DCS (au)
0.2	4.19	0.425	2.48	4.18	0.328	1.76
0.3	5.16	0.323	1.26	5.15	0.273	0.975
0.4	5.97	0.240	0.702	5.97	0.224	0.600
0.5	6.69	0.183	0.428	6.69	0.183	0.393
0.6	7.34	0.148	0.288	7.33	0.150	0.268
0.7	7.93	0.125	0.210	7.93	0.123	0.188
0.8	8.48	0.111	0.163	8.48	0.105	0.140
0.9	9.00	0.0974	0.127	9.00	0.0909	0.108
1.0	9.50	0.0891	0.104	9.50	0.0800	0.0859
1.2	10.4	0.0814	0.0794	10.41	0.0656	0.0587
1.4	11.3	0.0752	0.0628	11.25	0.0577	0.0442
1.6	12.0	0.0710	0.0519	12.0	0.0533	0.0358
1.8	12.8	0.0668	0.0434	12.8	0.0505	0.0301
2.0	13.5	0.0633	0.0371	13.5	0.0483	0.0259

Table 2. Small angle (0°–4.18°) contribution to the ICSs (10^{-17} cm^2) for the dipole-allowed transitions in e–N_2 scattering at 500 eV.

State	b $^1\Pi_u$	b′ $^1\Sigma_u^+$	c $^1\Pi_u$	c′ $^1\Sigma_u^+$	o $^1\Pi_u$
σ(0°–4.18°)	0.7635	0.4429	0.8406	0.7510	0.2304

equation. The results for columns 4 and 7 are 0.4278×10^{-17} cm^2 and 0.3425×10^{-17} cm^2, respectively. Therefore, the ICS to the lowest five dipole-allowed transitions from $\theta = 4.18^\circ$ to 13.5° is $(0.4278 + 0.3425) \times 10^{-17} = 0.7703 \times 10^{-17}$ cm^2. The ICSs from angles larger than 13.5° are negligibly small at 500 eV. Finally, after adding the contribution to the ICS from small and large angles, the ICS for all five states in e–N_2 collision at 500 eV is $(3.028 + 0.7703) \times 10^{-17} = 3.798 \times 10^{-17}$ cm^2. This indicates that most of the contribution to the ICS, almost 80% in this example, is from the range of scattering angles 0° to 4.18°. In this region we had to use the extrapolating function to calculate the contribution to the ICS because the experiment could not obtain data.

The above method used the DCSs measured at 500 eV. Therefore, it can only evaluate the ICS at this energy. The ICSs at other energies have been calculated using equations (4)

and (6). Vibrational states, whose excitation energies are below 13.6 eV, are covered in the measurement of the 12.85 eV band. The sum of the OOSs from these states is 0.6292 au. The remainder contributes to the measurement of the 13.99 eV band whose OOSs sum is 0.3964. The OOS is 0.3964. The Lassettre equation with two OOSs as input data is obtained using a least-squares fitting process to column 3 and column 6 in table 1. For column 3 the equation is

$$f_b(K^2) = \frac{0.6292}{(1+x)^6}\left[1 + 5.525\left(\frac{x}{1+x}\right) - 72.00\left(\frac{x}{1+x}\right)^2 + 299.9\left(\frac{x}{1+x}\right)^3 - 518.7\left(\frac{x}{1+x}\right)^4 + 475.1\left(\frac{x}{1+x}\right)^5\right]. \tag{9}$$

For column 6 the equation is

$$f_c(K^2) = \frac{0.3964}{(1+x)^6}[1 + 7.385\left(\frac{x}{1+x}\right) - 35.45\left(\frac{x}{1+x}\right)^2 + 157.0\left(\frac{x}{1+x}\right)^3 - 494.4\left(\frac{x}{1+x}\right)^4 + 741.2\left(\frac{x}{1+x}\right)^5\Big] \tag{10}$$

where $f_b(K^2)$ and $f_c(K^2)$ are the GOSs for the 12.85 eV band and the 13.99 eV band, respectively, and $\alpha = 1.518$ for equation (9) and 1.412 for equation (10). Errors between (9) and the experimental data are less than 2.9%. Most data have errors of less than 1%. The sum of all squared errors is 3.5×10^{-5}. Errors between (10) and the experimental data are less than 1.4% and the total squared errors is 5.3×10^{-6}. The ICSs for the transition to the lowest five dipole-allowed electronic states in e–N_2 scattering in the energy range of 200 to 1000 eV have been obtained using (6) and are given in the table 3.

Table 3. The ICSs for the lowest five dipole-allowed transitions in e–N_2 scattering.

Energy (eV)	$\sigma(10^{-16}\text{cm}^2)$
200	0.7903
250	0.6786
300	0.5968
350	0.5342
400	0.4845
450	0.4441
500	0.4105
550	0.3819
600	0.3575
650	0.3363
700	0.3176
750	0.3011
800	0.2864
850	0.2732
900	0.2612
950	0.2503
1000	0.2404

At 500 eV the ICS from the first method is 3.798×10^{-17} cm^2. This value agrees very well with the 4.105×10^{-17} cm^2 obtained by the second method. As the results in the first method include only the contribution between 0° and 13.5° better agreement is expected

if we add the neglected small contribution from the angles larger than 13.5° to the first method.

The first method allowed us to evaluate the contributions to the ICS from small angles (0°–4.18°) and large angles (4.18°–13.5°). The results indicated that almost 80% of the ICS is from scattering angles 0°–4.18° at 500 eV. Clearly the ICS receives a significant contribution mainly from small angles, particularly when the impact energies are high. This conclusion agrees with our previous calculation (Chen and Msezane 1995) for other reactions. Normally, researchers evaluate the ICS from a set of the DCS data. They extrapolate the data to the 0° by continuing the slope between the last two measured points, or use a slope which is approximately three (or five) times steeper than the slope achieved from continuing the last two measured points. As they estimated the slopes to the 0° the ICS obtained in their calculation is bound to contain large uncertainties. Our calculations indicate that a reliable extrapolation function, such as the universal extrapolation function or Lassettre's equation, is necessary in the ICS evaluation to avoid the errors caused by estimating the contribution from small angles. These calculations should also encourage and guide experimentalists to perform the DCS measurement at the smaller scattering angles. The second calculation allowed us to evaluate the ICSs at other energies as long as the impact energy is high enough and the Born approximation is applicable.

4. Conclusion

ICSs have been calculated for the lowest five dipole-allowed transitions in e–N_2 collision in the impact energy range from 200 to 1000 eV. The results demonstrate that at 500 eV almost 80% of the ICS is from scattering angles 0°–4.18°. In this region we used the extrapolation function to evaluate the contribution to the ICS. Therefore, a reliable extrapolation function, such as the universal extrapolation function or Lassettre's equation, is necessary in the calculation of the ICS from the DCS measurement in order to avoid the large uncertainties.

Acknowledgments

Research was supported by the US DoE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research and the Air Force Office of Scientific Research.

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