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Electron impact cross sections for $v = 0 \rightarrow 1$ vibrational excitation of N_2 at electron energies from 3 to 30 eV

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Abstract. Normalised, absolute electron impact differential cross sections (DCS) for the $(0 \rightarrow 1)$ vibrational excitation of N_2, for incident electron energies from 3 to 30 eV, have been measured with the help of a crossed beam apparatus over the angular range of 20 to 130°. The $l = 3$ (f wave) contribution was found to dominate the vibrational excitation at incident energies in the range 18 to 25 eV. From the DCS, the integral and momentum transfer cross sections were calculated. It could also be verified that the enhanced vibrational excitation due to the σ_u shape resonance has a peak value at about 21 eV with a full width at half maximum of about 7 eV. The DCS and the integral cross sections are compared with recent theoretical calculations of the converged rotational close coupling and the vibrational sudden approximation, as well as with the continuum multiple-scattering method.

1. Introduction

Vibrational excitation of N_2 by electrons with impact energies of 3 to 30 eV plays an important role in a variety of atmospheric phenomena as well as gas discharges containing N_2 and, as a consequence, accurate electron impact cross sections of N_2 are needed to understand and model the behaviour of those systems.

The N_2 shape resonance at 2.4 eV impact energy associated with the ${}^2\Pi_g$ state of N_2^- has been studied experimentally and theoretically in great detail, for both elastic scattering and for vibrational excitation (Schulz 1973, 1976, Krauss and Mies 1970, Chandra and Temkin 1976a, b, Dubé and Herzenberg 1979, Schneider *et al* 1979). Wong and Schulz (1975) measured the vibrational excitation of N_2 with impact energies of 4–10 eV at scattering angles of 25, 50, and 90°, and found them associated with a core-excited resonance at 8 eV. Trajmar and co-workers (Truhlar *et al* 1976) also determined normalised, absolute DCS, integral and momentum transfer cross sections for the vibrational excitation at the scattering angles of 20–135°, and at impact energies of 5 and 10 eV. At energies from 11 to 30 eV, the resonant enhancement of vibrational excitation was observed first in the DCS over the scattering angles of 25 to 90° by Pavlovic *et al* (1972) and recently reconfirmed by Tronc *et al* (1980). Away from resonances, at energies from 20 to 75 eV, vibrational excitation DCS have been quantitatively studied by Trajmar and co-workers (Truhlar *et al* 1972, 1977). Absolute

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DCS, integral and momentum transfer cross sections, however, have been measured only at very few energies in the energy range less than 30 eV.

In the present article, we report extensive normalised, absolute measurements of the DCS of the first excited vibrational state in the energy range 3 to 30 eV, and in the angular range 20 to 130°. For each impact energy, the DCS was integrated to obtain integral and momentum transfer cross sections. The main results are: (a) The angular distributions are characteristic of an f wave ($l = 3$) resonance; (b) A significant peak in the integral and momentum transfer cross sections was observed at about 21 eV. This results from the f wave resonant enhancement of the vibrational excitation, and confirms earlier DCS measurements taken by Pavlovic *et al* (1972) at scattering angles of 25 to 90°; (c) The present results are compared with recent calculations of the converged rotational close coupling and the vibrational sudden approximation with an effective potential (Onda and Truhlar 1979, 1980), as well as of a single-particle shape resonance in the continuum multiple-scattering method (Dehmer *et al* 1980, Dehmer 1980), and are found to show a fairly good overall agreement.

2. Experimental methods

Our apparatus uses a crossed electron beam and molecular beam scattering technique. An energy-selected electron beam of the desired impact energy E_0 from an electrostatic monochromator is collimated and focused by an electrostatic lens system at right angles onto the target molecular beam. The electrons scattered at an angle θ with respect to their incident direction are energy selected by an analyser and counted by a channeltron detector.

The energy-discriminating element of the monochromator is a 127° electrostatic cylindrical deflector with mean radius of 25 mm and entrance and exit slits of 0.3 mm. A lens system focuses the electron emitted by a thoria-coated iridium filament onto the entrance slit of the monochromator. The electron beam from this monochromator has an energy width of 50 meV (FWHM), and a current of 10^{-9} A. A second lens system accelerates the electrons to the desired impact energy and focuses them onto the molecular beam of N_2. A Faraday cup monitors the incident electron intensity.

The molecular beam of N_2 with a density corresponding to a pressure of about 10^{-3} Torr is formed by effusion from a nozzle having a backing pressure of about 0.5 Torr.

Electrons scattered from the molecular beam are first selected by slits with an acceptance angle of 2° and then focused by a third lens system onto the entrance slit of the analyser. In order to keep the transmission efficiency as constant as possible the analyser, which is essentially a repetition of the monochromator, incorporates accelerating/decelerating electron lenses and slits to adjust the analysing energy to about 1 eV. The energy loss of about 0.3 eV is relatively small when compared with the energy of elastically scattered electrons so that the analyser works essentially under constant conditions. (The transmission efficiency of the analyser normally depends upon the energy of the electrons. An alternative solution would be to calibrate the transmission efficiency of the vibrational excitation in the entire energy-loss region of interest.) The analyser can be rotated through the angular range 20 to 140°.

All parts of the spectrometer are constructed from molybdenum and non-magnetic stainless steel; parts are insulated from one another by fused quartz. Magnetic fields in the region of the spectrometer are reduced to about 10 mG by a double mu-metal shield enclosed in the vacuum chamber. The non-magnetic stainless-steel vacuum chamber is evacuated by a 6 in mercury diffusion pump with a cold water baffle and a liquid nitrogen trap. The background pressure in the vacuum chamber during the present measurements was typically 1×10^{-5} Torr with the target beam on.

The overall resolution during these measurements was 50 meV. This is sufficient to separate clearly the $v = 0 \to 1$ excitation from the $v = 0 \to 0$ (elastic) and the $v = 0 \to 2$ excitation, but insufficient to resolve any rotational structures. The electron energy scale was calibrated by measurement of the 19.3 eV resonance in He.

Figure 1 shows a typical energy-loss spectrum of N_2 at 3 eV. From the experimental data, the ratio $R_1(E_0, \theta) = I_{01}/I_{00}$ $(\sigma_{01}/\sigma_{00})$ of the peak heights of the $v = 0 \to 1$ vibrational excitation cross section (I_{01}) to the elastic-scattering one (I_{00}) was determined. To obtain a normalised, absolute value of the vibrational excitation DCS (σ_{01}), $R_1(E_0, \theta)$ was multiplied by the absolute elastic DCS (σ_{00}) of N_2 obtained at exactly the same incident energy and scattering angle.

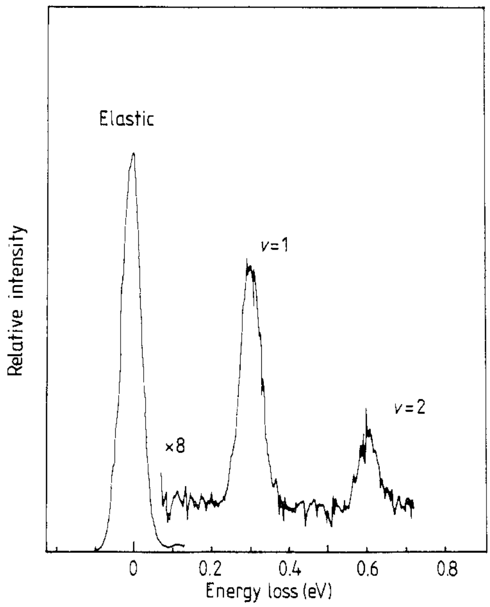

Figure 1. Energy-loss spectrum of N_2 at an impact energy of 3 eV and scattering angle of 30°. The feature corresponding to vibrationally inelastic scattering to the first excited vibrational state is labelled $v = 1$.

3. Results and discussion

Values of $R_1(E_0, \theta)$ were obtained at incident energies of 3, 5, 7.5, 10, 15, 18, 20, 22.5, 25 and 30 eV. The angular range was 20–130° in steps of 10° for all energies. As expected, the energy resolution was not high enough to resolve the pure rotational transitions in N_2. Results of the present measurements are given in table 1. The ratios $R_1(E_0, \theta) = I_{01}/I_{00}$ $(\sigma_{01}/\sigma_{00})$ are given in parentheses. Srivastava *et al* (1976) have measured the ratio of σ_{00} for N_2 to that of He for an angular range 20–135° at incident energies of 5–75 eV. To obtain the renormalised DCS for N_2, those ratios were multiplied by the latest measurements of e + He elastic scattering DCS by Register *et al* (1980). Values of the DCS at 7.5, 18, 22.5 and 25 eV were obtained by interpolating their results between 7 and 10 eV, 15 and 20 eV, and 20 and 30 eV, respectively.

Table 1. Absolute differential $\sigma_{01}(E_0, \theta)$, integral σ_I and momentum transfer σ_M cross sections for $v = 0 \rightarrow 1$ vibrational excitation in N_2. Units are 10^{-19} cm^2 sr^{-1} in σ_{01}, and 10^{-18} cm^2 in σ_I and σ_M. In parentheses are the ratios $R_1(E_0, \theta)$ in units of 10^{-3}. Errors in $\sigma_{01}(E_0, \theta)$ are 19% (3 eV), 21% (5 eV), 25% (7.5 and 15–30 eV), and 40% (10 eV). Errors in σ_I are 20% (3 eV), 22% (5 eV), 26% (7.5 and 15–30 eV), and 41% (10 eV), and those in σ_M are 24% (3 eV), 25% (5 eV), 29% (7.5 and 15–30 eV), and 42% (10 eV).

E_0 / θ	3	5	7.5	10	15	18	20	22.5	25	30
20	216	10.3	—	—	6.46	—	25.8	—	15.2	7.74
	(63.4)	(6.47)			(1.74)		(5.68)		(3.16)	(1.59)
30	138	8.99	4.82	1.93	4.63	14.8	19.3	20.7	9.29	3.24
	(41.2)	(5.55)	(2.41)	(0.837)	(1.81)	(5.51)	(7.04)	(7.66)	(3.56)	(1.36)
40	109	6.86	3.76	1.44	3.05	5.48	14.1	8.87	7.29	2.88
	(27.5)	(4.21)	(1.86)	(0.696)	(1.80)	(3.91)	(8.82)	(5.91)	(5.40)	(2.53)
50	75.2	4.86	2.68	1.65	3.64	4.64	9.89	6.82	5.42	2.30
	(34.8)	(3.35)	(1.23)	(0.816)	(2.84)	(4.30)	(10.2)	(8.12)	(7.23)	(3.77)
60	72.7	4.00	3.14	1.20	3.25	4.76	10.8	7.78	5.83	1.83
	(44.9)	(3.42)	(2.36)	(0.977)	(3.74)	(6.52)	(17.2)	(13.9)	(12.4)	(5.54)
70	94.0	3.91	3.18	1.16	2.92	4.69	8.78	4.70	4.90	1.52
	(77.1)	(4.44)	(2.34)	(1.30)	(5.21)	(13.4)	(22.5)	(17.4)	(21.3)	(8.46)
80	115	5.40	2.38	0.961	3.64	4.72	6.73	5.02	4.22	1.50
	(116)	(7.50)	(2.97)	(1.55)	(10.4)	(16.3)	(26.9)	(22.8)	(22.2)	(11.5)
90	121	4.04	1.79	0.518	2.48	3.84	5.55	5.48	2.91	1.20
	(136)	(6.73)	(3.09)	(1.15)	(8.87)	(17.4)	(29.2)	(32.2)	(20.8)	(10.9)
100	124	3.72	1.05	0.405	2.81	3.51	7.32	8.72	4.28	1.22
	(145)	(6.52)	(1.95)	(0.901)	(7.40)	(14.7)	(27.1)	(25.6)	(14.8)	(9.38)
110	81.8	3.18	1.00	0.419	2.01	4.31	10.6	7.48	5.12	1.13
	(95.2)	(5.58)	(1.81)	(0.762)	(4.38)	(10.5)	(27.1)	(18.7)	(18.3)	(6.25)
120	57.4	2.60	1.00	0.505	1.67	4.57	11.0	9.17	5.50	1.33
	(63.6)	(4.48)	(1.51)	(0.841)	(2.93)	(9.94)	(21.9)	(20.8)	(14.1)	(5.13)
130	59.0	3.26	1.05	—	1.39	5.43	15.5	10.4	7.75	1.92
	(59.0)	(5.26)	(1.38)		(1.98)	(8.35)	(25.0)	(18.6)	(14.9)	(4.93)
σ_I	123	6.10	3.12	1.53	3.86	7.55	19.5	12.6	8.22	2.66
σ_M	114	5.34	2.40	1.44	3.38	6.51	22.8	11.7	8.14	2.24

Errors in the values of $R_1(E_0, \theta)$ were estimated from the reproducibility of 2–4 separate measurements of R taken on different days under different spectrometer conditions. The maximum relative error was 12% at 3 eV, 15% at 5 eV, 20% at 7.5 eV and 15–30 eV, and 38% at 10 eV. Relative errors of σ_{01} were determined by the sum of the squared relative errors of R_1 and σ_{00}. The relative error of σ_{00} (Srivastava *et al* 1976) was 15% at 5–30 eV. This gives the following estimated relative maximum errors for σ_{01}: 19% at 3 eV, 21% at 5 eV, 25% at 7.5 and 15–30 eV, and 40% at 10 eV.

Figure 2 shows σ_{01} as a function of the scattering angles and incident energies. Also shown are previous experimental values of Ehrhardt and Willmann (1967) at 2.8 eV, Trajmar and co-workers (Truhlar *et al* 1976, 1977, Onda and Truhlar 1980) at 5, 10, 20 and 30 eV, and Pavlovic *et al* (1972) at 18, 20, 22.5 and 25 eV. Since the experimental data of Ehrhardt and Willmann (1967) were given in arbitrary units, they were normalised to the present measurements at the scattering angle of 90°. Within the limits of the experimental errors, all normalised DCS are in satisfactory agreement with the present measurements, both in shape and magnitude, except for the results at 20 and 30 eV.

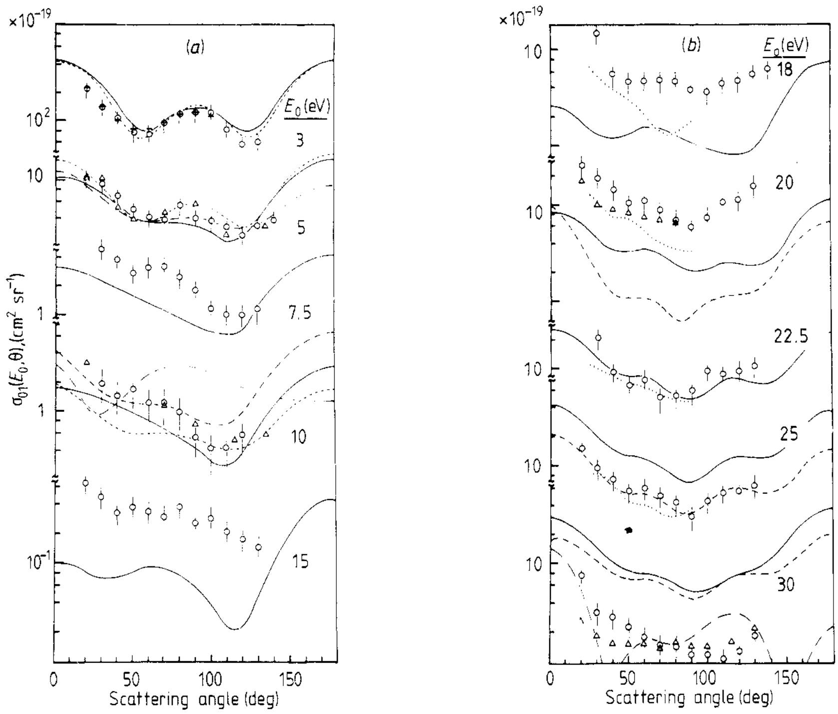

Figure 2. Differential cross sections for the $v = 0 \rightarrow 1$ vibrational excitation in N_2 between (*a*) 3 and 15 eV and (*b*) 18 and 30 eV. ○, present measurements; +, Ehrhardt and Willmann (1967), their data normalised to present results at 90°; △, Trajmar and co-workers (1976); ——, Dehmer and co-workers (Dehmer 1980); - - - -, Chandra and Temkin (1976a, b); — · — · —, Truhlar *et al* (1976); — — —, Onda and Truhlar (1979); · · · ·, Pavlovic *et al* (1972); △, Trajmar and co-workers (Truhlar *et al* 1972, 1977); – – –, Onda and Truhlar (1980).

Recent theoretical results of Dehmer and co-workers (Dehmer 1980) are given in figure 2. DCS calculations of vibrational excitation using the multiple-scattering method in the adiabatic approximation were recently carried over the wide energy range from threshold to 50 eV. Also shown in figure 2 are the theoretical results of Truhlar *et al* (1976, 1977), Onda and Truhlar (1979, 1980), and Chandra and Temkin (1976a, b). The data at 3 eV indicate that the strong resonance (at 2.4 eV) still enhances the vibrational excitation. The angular distribution of the electrons excited from $v = 0 \rightarrow 1$ shows clearly the contribution of a d wave ($l = 2$). Hybrid theory was used in the Chandra and Temkin (1976a) calculation including only the $^2\Pi_g$ symmetry. One finds fair agreement between experiment and theory. At 5 eV, the measured cross sections agree with the calculations of Dehmer and co-workers (Dehmer 1980), Truhlar *et al* (1976), and Chandra and Temkin (1976b) within the experimental error. Truhlar *et al* (1976) used a model interaction potential with adjustable parameters in unconverged rotational–vibrational close coupling calculations. On the other hand, Chandra and Temkin (1976b) included the contribution of non-resonant symmetries in their hybrid theory. At 10 eV, however, both the calculations of Truhlar *et al* (1976) and Chandra and Temkin (1976b) differ and neither agrees well with the measurements. Here the DCS is so small that a large error of 40% is not surprising. Onda and Truhlar (1979) have recently reported calculations using an effective potential with no semi-empirical parameters at 10 and 50 eV (see figure 2). The calculations essentially employed the converged rotational close coupling and vibrational sudden approximations, and the effective potential involved a static plus polarisation potential and exchange. Among the theoretical calculations, the results of Dehmer and co-workers (Dehmer 1980), as well as those of Onda and Truhlar (1979), are closest to measurements. At 7.5 and 15 eV, the present results are also compared with those of Dehmer and co-workers (Dehmer 1980) for which the agreement in shape is good, but the theoretical results are generally much too small.

A major feature of the present measurements is the angular distribution of the vibrational excitation DCS between 18 and 25 eV. At 18–25 eV, the distribution exhibits a minimum at about 45°, followed by a local maximum at about 65° and a slightly deeper minimum at 90°. These shapes are characteristic for an f wave ($l = 3$) resonance, and are consistent with the theoretical calculations of Dehmer *et al* (1980), Dehmer (1980) and Onda and Truhlar (1980). The calculation of Dehmer *et al* (1980) predicted a gross enhancement of the integrated vibrational excitation cross section in the 15–35 eV range, centred at 26 eV, arising from a broad shape resonance of σ_u symmetry. This feature is more readily apparent in the recent DCS calculation which appears to be mainly an f wave ($l = 3$) component of the σ_u. In the laboratory frame coordinate system employed by Onda and Truhlar (1980), it also corresponds to the orbital angular momentum with $l = 3$ and, for scattering by the ground state, to total angular momentum $J = 3$. Their calculation include background contributions. The agreement is best at 22.5 eV (Dehmer and co-workers) and 25 eV (Onda and Truhlar), both in shape and magnitude. As shown in figure 2, the vibrational excitation DCS measured by Pavlovic *et al* showed various structures as a function of θ and E_0 over the angular range from 25 up to 90° and the energy range 20–25 eV. Our measurements give no indication of structures at these energies.

The results also confirm what Onda and Truhlar indicated in their paper, namely that they possibly underestimated the vibrational excitation DCS at 20 eV, and overestimated it at 30 eV, because their calculated resonance energy at 30 eV was too high. At 30 eV, the data indicate that the f wave shape is no longer dominant, and thus poor agreement with the theoretical values is to be expected. The above is also applicable to explain the discrepancy of absolute magnitudes between the present DCS measurement and the theoretical result of Dehmer and co-workers.

Also shown in table 1 are the integral (σ_I) and momentum transfer (σ_M) cross sections calculated from the equations

$$\sigma_I = 2\pi \int_0^\pi \sigma_{01}(N_2, \theta) \sin\theta \, d\theta \tag{1}$$

and

$$\sigma_M = 2\pi \int_0^\pi \sigma_{01}(N_2, \theta)\left(1 - \frac{k_1}{k_0}\cos\theta\right) \sin\theta \, d\theta \tag{2}$$

where k_0 and k_1 are the magnitudes of the initial and final momenta of the electron, respectively. Since the experimental DCS are not available over the whole angular range, some extrapolations were necessary in order to carry out the integrations in equations (1) and (2). Three methods were used: (a) At 3 eV, the shape of the hybrid calculations of Chandra and Temkin (1976a) were used for the low- and high-angle extrapolations. (b) For 5–30 eV, the most accurate calculations available today, namely those of Truhlar *et al* (1976, 1977, 1979) and Onda and Truhlar (1980) at 5, 10, 20, 25 and 30 eV, were used. From the close resemblance in shape of the DCS between 7.5 and 10 eV, as well as between 20 and 25 eV, the DCS for low ($\theta < 20°$) and high ($\theta > 140°$) angles were obtained by using the extrapolations of the theoretical DCS of 10 and 25 eV, respectively. (c) For 3–30 eV, and recent DCS calculations of Dehmer and co-workers (Dehmer 1980) were also used as a guide to the extrapolation. The estimated errors in σ_I are 20% at 3 eV, 22% at 5 eV, 26% at 7.5 and in the range 15–30 eV, and 41% at 10 eV, and those in σ_M are 24% at 3 eV, 25% at 5 eV, 29% at 7.5 and 15–30 eV, and 42% at 10 eV. These errors are based on the error of the DCS itself, and on an estimate of the extrapolation error (7% in σ_I and 14% in σ_M) from 0 to 20° and from 140 to 180°.

The integral and momentum transfer cross sections are given in figure 3. They confirm a resonance which was observed earlier in the DCS measurements by Pavlovic *et al* and Tronc *et al* (1980). Pavlovic *et al* (1972) interpreted this hump as a resonance

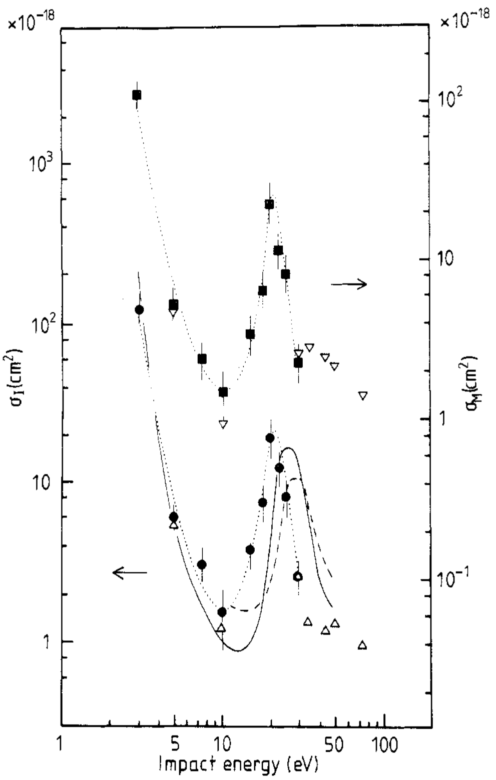

Figure 3. Integral (σ_I) and momentum transfer (σ_M) cross sections for $v = 0 \rightarrow 1$ vibrational excitation in N_2. ●, ■, present results; △, ▽, Trajmar and co-workers (1977); ——, Dehmer *et al* (1980); — — —, Onda and Truhlar (1980).

associated with doubly excited states of the target. The above-mentioned calculations of Dehmer *et al* (1980) and Onda and Truhlar (1980), however, show the enhancement to arise simply from a single-particle shape resonance associated with the (σ_u 2p) orbital. Both calculations are given in figure 3. The calculation of Dehmer *et al* (1980) shows a peak value at 26.5 eV, which is in better agreement with the measurements at 21 eV than the Onda and Truhlar (1980) calculations of 30 eV. The full width at half maximum is 7 eV in the present measurement. At incident energies less than 3 eV, the $v = 0 \rightarrow 1$ cross sections increase steeply, a result which is due to the $^2\Pi_g$ resonance at an energy of about 2.4 eV.

4. Conclusion

The above measurements provide a broad range of quantitative data for the vibrational excitation $v = 0 \rightarrow 1$ over an angular range 20 to 130°, and an energy range 3–30 eV, and its corresponding integral and momentum transfer cross sections. It could also be confirmed experimentally that the enhanced vibrational excitation due to the σ_u shape resonance has a peak value of 21 eV. The characteristic f wave shape is also clearly observable.

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References

Chandra N and Temkin A 1976a *Phys. Rev.* A **13** 188–203
—— 1976b *J. Chem. Phys.* **65** 4537–39
Dehmer J L 1980 private communication (N_2 vibrational DCS results)
Dehmer J L, Siegel J, Welch J and Dill D 1980 *Phys. Rev.* A **21** 101–4
Dube L and Herzenberg A 1979 *Phys. Rev.* A **20** 194–213
Ehrhardt H and Willmann K 1967 *Z. Phys.* **204** 462–88
Krauss M and Mies F H 1970 *Phys. Rev.* A 1592–8
Onda K and Truhlar D G 1979 *J. Chem. Phys.* **71** 5107–23
– — 1980 *J. Chem. Phys.* **72** 5249–62
Pavlovic Z, Boness M J W, Herzenberg A and Schulz G J 1972 *Phys. Rev.* A **6** 676–85
Register D F, Trajmar S and Srivastava S K 1980 *Phys. Rev.* A **21** 1134–51
Schneider B L, Le Dourneuf M and Vo Ky Lan 1979 *Phys. Rev. Lett.* **43** 1926–9
Schulz G J 1973 *Rev. Mod. Phys.* **45** 423–86
—— 1976 *Principles of Laser Plasmas* ed G Be Kefi (New York: Wiley) pp 33–88
Srivastava S K, Chutjian A and Trajmar S 1976 *J. Chem. Phys.* **64** 1340–4
Tronc M, Azria R and Le Coat Y 1980 *J. Phys. B: At. Mol. Phys.* **13** 2327–32
Truhlar D G, Brandt M A, Chutjian A, Srivastava S K and Trajmar S 1976 *J. Chem. Phys.* **65** 2962–9
Truhlar D G, Brandt M A, Srivastava S K, Trajmar S and Chutjian A 1977 *J. Chem. Phys.* **66** 655–69
Truhlar D G, Onda K, Eades R A and Dixon D A 1979 *Int. J. Quantum Chem.: Quantum Chemistry Symposium* **13** 601–32
Truhlar D G, Trajmar S and Williams W 1972 *J. Chem. Phys.* **57** 3250–9
Wong S F and Schulz G J 1975 *Bull. Am. Phys. Soc.* **20** 240