

Origin of enhanced vibrational excitation in N_2 by electron impact in the 15–35 eV region

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(Received 12 March 1979)

The authors calculate the integrated vibrational excitation cross section for $e-N_2$ scattering in the interval 0–50 eV using the continuum multiple-scattering model with the Hara exchange approximation. Resonant enhancement is observed at 2.4 eV owing to the well-known π_g shape resonance. In addition, however, enhanced vibrational excitation is found centered at ~ 26 eV, arising from a broad shape resonance in the σ_u channel. The authors propose this one-electron feature as the main source of the enhanced vibrational excitation observed by Pavlovic *et al.* in the 15–35 eV region.

Several years ago, Pavlovic, Boness, Herzenberg, and Schulz¹ reported that “the vibrational cross section by electron impact on N_2 exhibits a broad maximum near 22 eV.” Prompted by the great width (full width at half maximum > 5 eV) and the complex energy dependence of the differential cross section, those authors interpreted this enhanced vibrational excitation in terms of a large manifold of “overlapping compound states above 20 eV,” including possible shape resonances and singly and multiply core-excited Feshbach resonances. In this paper we document our earlier proposal² that a very simple, one-electron mechanism—a σ_u shape resonance—plays a central role in the observations of the above authors. At the very least, this resonance is shown to be responsible for the gross enhancement of vibrational excitation in the 15–35-eV range. The extent to which it accounts for the energy dependence of the corresponding differential cross section (DCS) is currently under investigation and will be reported separately. The possible role of the σ_u resonance was anticipated by Pavlovic *et al.*,¹ but they had insufficient theoretical information to identify its primary role. This interpretation suggested itself to us during an earlier study³ of $e-N_2$ scattering using the continuum multiple-scattering model^{4,5} (CMSM) with Slater exchange. That work identified weak intermediate-energy resonances in the σ_u and δ_g channels, in addition to the well-known π_g resonance⁶ at 2.4 eV. More recent work⁷ employing the CMSM with the Hara exchange approximation⁸ has proven to be considerably superior but indicates the same three resonances; only the σ_u and δ_g features were weaker, especially the δ_g . This is consistent with recent total electron scattering measurements⁹ on N_2 , which indicate a very weak, broad feature at 22 eV, corresponding to the

σ_u resonance, and no sign of the δ_g resonance at ~ 13 eV. Notwithstanding the extreme weakness of these intermediate-energy features in the elastic scattering cross section, we felt they might be important in alternative scattering channels, such as vibrational excitation. Below we show that the σ_u is, indeed, important in this role, whereas the δ_g is not, owing to its weakness and off-axis orientation. Results for vibrational excitation due to the strong π_g resonance are also presented.

The cross section for vibrational excitation by electron impact, in the adiabatic-nuclei approximation, is given by¹⁰

$$\sigma(v_f \leftarrow v_i) = \pi(E_f/E_i)^{1/2} E_i^{-1} \times \sum_{LL'} \left| \int dR \chi_{v_f}^*(R) T_{LL'}(R) \chi_{v_i}(R) \right|^2, \quad (1)$$

where L denotes the double index (l, m) , χ_{v_i} and χ_{v_f} are the initial and final vibrational wave functions, E_i and E_f are the kinetic energies of the scattered electron before and after the vibrational transition, and $T_{LL'}(R)$ is the T -matrix element defined by

$$T_{LL'}(R) \equiv \delta_{LL'} - S_{LL'}(R), \quad (2)$$

in terms of the S matrix $S_{LL'}(R)$, both of which depend parametrically on the internuclear separation R . For vibrationally elastic collisions, $v_i = v_f$, the effect of Eq. (1) is to compute the cross section on the basis of an R -averaged transition amplitude, obtained by simply averaging T -matrix elements computed at different fixed values of R , weighted by the probability of the molecule being at each R . For $v_i \neq v_f$, the cross section for the corresponding vibrational transition is obtained. In the present work, nine equally spaced values of

R between $1.874a_0$ and $2.274a_0$ define the mesh of internuclear distances, and the vibrational wave functions were approximated by harmonic-oscillator functions, as only the first four vibrational levels were treated. Otherwise, the specifics of the CMSM calculation were precisely the same as those used and documented in Ref. 7. Note particularly that variation of the polarizability with internuclear distance was not taken into account. This is not expected to significantly affect the present results as the σ_u resonance has been shown⁷ to be insensitive to the polarization potential at $R=R_e$. Nevertheless, assessment of the quantitative effects of this approximation warrants future study.

Our results are shown in Fig. 1. The vibrationally elastic results ($0-0$) have been discussed elsewhere.⁷ Here we only note that although the π_g resonance is prominent, the bulk of the cross section is made up of nonresonant contributions. By contrast, vibrational excitation is overwhelmingly dominated by resonant processes. In Figs. 1(b)–1(d), the total cross section is indistinguishable from the resonant π_g (2.4-eV) and σ_u (26-eV) partial cross sections, indicating that nonresonant processes are negligible. Similarly, the weak δ_g shape resonance located at ~ 13 eV is ineffective

in enhancing vibrational excitation since it is not a strong, localized resonance (like the π_g), nor an axially oriented resonance (like the σ_u) and therefore couples only weakly with the nuclear motion.

Vibrational excitation via the π_g resonance is a well-known and often-studied process^{6,11-14}; therefore although it is not the main focus of this article, we will comment briefly on the comparison of these results with the earlier work. The shape of the π_g resonance (in vibrationally elastic and inelastic channels alike) is known to have a vibrational substructure owing to the comparable resonance lifetime and vibrational period. Our model presently neglects vibrational close coupling, studied extensively by Chandra and Temkin¹³ and others,^{11,12,14} so that we must compare our results with an average of the peaks and valleys in the experimental spectrum. Our peak values of 3.6, 1.8, and 1.0 \AA^2 for the ($0-1$), ($0-2$), ($0-3$) transitions, respectively, agree well with a gross average of the oscillations in the vibrational substructure presented by Chandra and Temkin¹³ and lie somewhat above experimental values, although normalization of the latter remains in doubt and could be too low by as much as a factor of 2.^{12,13} Imposition of the vibrational structure by an energy-modified adiabatic approxi-

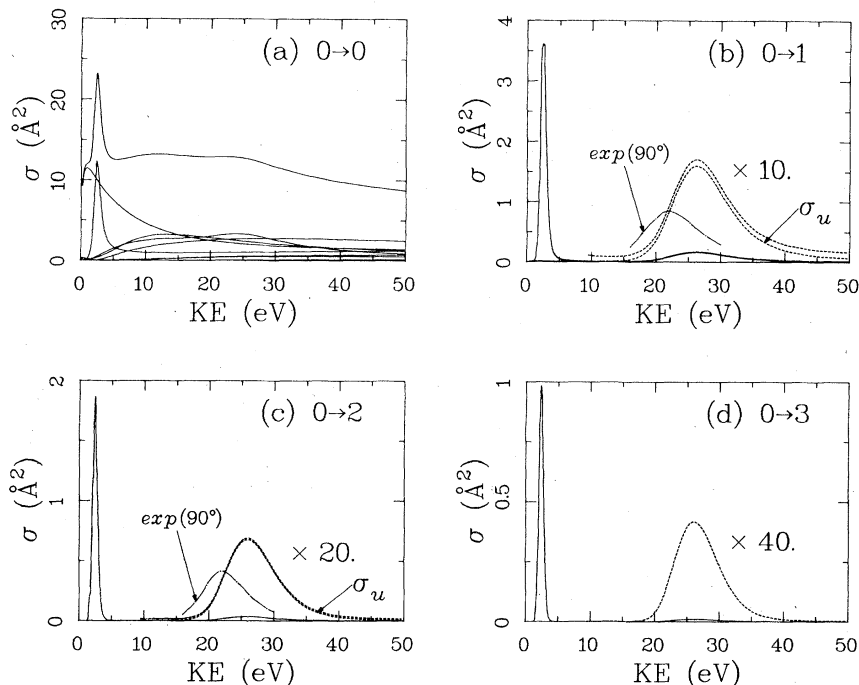


FIG. 1. Vibrationally elastic and inelastic cross sections for $e\text{-N}_2$ scattering from 0 to 50 eV. The dash-dot lines in Figs. 1(b) and 1(c) represent an estimate of the integrated vibrational excitation cross section given by $4\pi \times d\sigma(90^\circ)/d\Omega$ using DCS data from Fig. 2.4 of Ref. 12.

mation has been suggested by Nesbet¹⁴ and is under investigation.

The other major feature in the vibrational excitation spectra between 0–50 eV is a broad hump extending from ~15 to 40 eV centered at ~26 eV. This feature is due wholly to the weak but axially oriented σ_u shape resonance, and resembles the broad hump observed by Pavlovic *et al.*¹ Hence we propose this simple independent-electron mechanism as the origin of the enhanced vibrational excitation observed experimentally between 15 and 35 eV. Although this work establishes the main source of this enhancement, it simultaneously prompts further work on three issues. *First*, the vibrational excitation DCS must be calculated to determine to what extent the σ_u shape resonance accounts for the complex energy dependence observed experimentally. The possibility for this is suggested indirectly by unpublished calculations¹⁵ on vibrationally elastic e -SF₆ scattering in which we observe that the shape of the DCS changes significantly within the t_{1u} shape resonance at 7.2 eV as a consequence of an avoided crossing by two strongly repelling eigenphases. It is not clear that this will be the case for the σ_u resonance in e -N₂, as an avoided crossing does exist (between the p -dominated and the resonant, f -dominated eigenphases), but the interaction is weak and confined to a very narrow (~0.1 eV) spectral range. We hesitate to speculate further until the DCSs are calculated; however, one should keep in mind that some of the states discussed by Pavlovic *et al.*¹ could affect details of the vibrational-excitation DCS even though they are not needed to account for the gross enhancement in the corresponding integrated cross section. *Second*, a careful comparison of absolute magnitudes should be made. This will result from either the calculation of the DCS or the experimental measurement of the integrated cross section for vibrational excitation in the 15–35-eV range. Two sources of fragmentary information exist in the latter case: (i) A crude estimate of the integrated cross section is given in terms of the differential cross section by $4\pi d\sigma(90^\circ)/d\Omega$. Using this rule of thumb, we have converted the (0–1) and (0–2) DCS data given in Fig. 2.4 of Ref. 12 in the range 15–35 eV into approximate integrated cross sections and have included them in Fig. 1 as dash-dot lines. That the calculated σ_u enhancement in Figs. 1(b) and 1(c) is roughly comparable to and in fact exceeds the experimental estimates strongly suggests that the σ_u shape resonance accounts for the bulk of the vibrational excitation cross section in this region. The similarity of theoretical and experimental shapes in Figs. 1(b) and 1(c) also supports our interpretation. (ii) Experimental estimates of

0.10 Å² and 0.025 Å² for the (0–1) channel have been reported at 20 eV¹⁶ and 30 eV,¹⁷ respectively. Direct comparison with the present results (~0.05 Å² at 20 eV and ~0.11 Å² at 30 eV) yields poor agreement; however, including the 4-eV energy shift between the theoretical and experimental resonance positions yield theoretical values of ~0.14 Å² and ~0.05 Å². These values confirm the experimental trend, which suggests resonant enhancement near 20 eV, but are somewhat larger than experiment. Integrated cross sections on a finer mesh are sorely needed to make a definitive comparison with theory, as comparisons such as the one above involving two points in the vicinity of a resonance are unreliable. Theoretical values for the (0–1) integrated cross section, given in Ref. 17, indicate an increase between 30 and 35 eV which disagrees with the observed experimental trend; however, it is again difficult to judge qualitative trends on such a coarse energy mesh. *Third*, the discrepancy between the theoretical and experimental resonance positions is larger than that observed in our previous comparisons of intermediate-energy resonances in e -CO₂^{18,19} and e -SF₆²⁰ scattering (including treatment of vibrational excitation in e -CO₂¹⁹) and should be resolved. Ironically, use of the Slater exchange approximation in Ref. 3 gives a resonance position of ~22 eV, in agreement with experiment, although the Hara exchange approximation is more realistic in several other respects.

Finally, we would like to emphasize that many molecules are likely to have intermediate-energy (~10–40 eV) shape resonances, which are too weak to be clearly observed in elastic scattering, but which may be prominent in another observation channel such as vibrational excitation. We have already verified cases in N₂, CO₂^{5,18,19} OCS,¹⁸ CS₂,¹⁸ and SF₆.²⁰ It is often possible to predict this situation by comparing e -molecule scattering and (preferably) inner-shell molecular photoionization. These two processes frequently exhibit prominent features which are due to analogous resonant continuum states. However, owing to the extra electron in the scattering process, shape resonances in this case will be several volts (~10–15 eV) higher in the kinetic-energy spectrum. In the present case, the presence of the σ_u shape resonance was already hinted at by the K -shell photoionization spectrum of N₂,^{21,22} which exhibits a prominent f -type shape resonance in the σ_u channel at ~10-eV photoelectron energy. This connection was described in our earlier work³ on e -N₂ scattering. As another illustration, note that in L -shell photoionization^{23,24} of SF₆, shape resonances of t_{2g} and e_g symmetries are observed at 5 and 15 eV, respectively. As expected, we found²⁰

e -SF₆ shape resonances of the corresponding symmetries at 12.7 and 27 eV, in addition to a_{1g} and t_{1u} shape resonances at 2.1 and 7.2 eV which correspond to highly localized bound states in the field of neutral SF₆. This type of reasoning can be used to anticipate or verify the existence of weak shape resonances which may be difficult to observe in elastic scattering, but which may be important in other processes.

ACKNOWLEDGMENTS

This work was performed in part under the auspices of the U.S. DOE and was supported in part by NSF Grant No. CHE78-08707. Acknowledgment is also made to donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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