

Transmission effects in unfolding electronic-vibrational electron-molecule energy-loss spectra

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The results of an investigation concerning the sensitivity of conventional unfolding methods applied to electronic-vibrational electron-energy-loss spectra to the transmission efficiency of electron spectrometers are presented. This investigation was made in an effort to understand differences in the differential cross sections for excitation of low-lying electronic states determined experimentally by various groups using electronic-vibrational energy-loss spectra of N₂. In these experiments, very similar spectral unfolding methods were used, which relied on similar Franck-Condon factors. However, the overall analyses of the electron scattering spectra (by the individual groups) resulted in large differences among the differential cross sections determined from these energy-loss spectra. The transmission response of the experimental apparatus to different-energy scattered electrons has often been discussed as a key factor that caused these disagreements. The present investigation shows in contrast that the effect of transmission is smaller than that required to independently explain such differences, implying that other systematic effects are responsible for the existing differences between measurements.

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Electron-impact excitation of gaseous diatomic molecules such as H₂, N₂, O₂, NO, and CO plays a pivotal role in a host of environments such as in the earth's and other planetary atmospheres, in interstellar media, in man-made low-temperature plasmas, and in fusion tokamaks [1]. Electron-impact excitation, dissociation, and ionization ignite a chain of reactive processes involving the reactive species created [2]. In the case of H₂, N₂, and NO, spectral unfolding methods have been applied to electron-energy-loss spectra, which have resulted in elastic and excitation differential cross sections (DCSs) for important low-lying electronic states of these molecules. For most of these measurements the errors quoted are in the 20–25% region, but differences between these DCSs are in some cases a factor of 2 or more. It has been suggested that such differences may be due primarily to transmission response of the spectrometers employed to carry out these measurements.

High-resolution electron-impact molecular energy-loss spectra are composed of overlapping vibrational levels pertaining to different electronic states. In such cases, vibrational manifolds of individual electronic states have to be unfolded from the spectrum. Unfolding techniques for low-lying electronic states of molecules have exploited the Franck-Condon principle for the vertical (excitation) transition where these low-lying electronic states are of different symmetries and do not perturb each other. In the unfolding algorithm, an individual line function is determined from an isolated $X(v''=0) \rightarrow N(v')$ feature (i.e., from the ground-electronic-state X , $v''=0$ vibrational level to the N th-excited-state v' vibrational level). A composite function for each electronic excitation is then constructed from the linear superposition of individual line functions, weighted by their Franck-Condon factors. This composite function for each electronic state is fitted (via least squares) to the measured spectrum. This procedure greatly simplifies the unfolding algorithm, by reducing the number of fitting parameters

from the total number of vibrational levels observed in the spectrum to the number of electronic states plus several (usually <3) background terms. Such an unfolding method should be accurate as long as the vibrational line intensities in each electronic state remain strictly in proportion to their Franck-Condon factors. As long as perturbative effects due to nuclear or electronic coupling are small, any deviation from the Franck-Condon symmetry can be expected to be negligible. Even when the effects of second-order couplings such as spin-orbit or configuration interaction are included (as is the case for the low-lying electronic spectra in H₂, N₂, and NO studied), the Franck-Condon factor rule should in principle hold very well for such light diatomic targets (<5% variation, e.g., when N₂ is compared to Ne; see, e.g., Ref. [3]).

Recently, we carried out careful and extensive N₂ energy-loss measurements in the energy-loss range of 6.25 to 11.25 eV, which covered the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$, and $C^3\Pi_u$ states and determined DCSs for excitation of these electronic levels from the ground $X^1\Sigma_g^+$ ($v=0$) state [4]. These DCS data were determined at the incident electron energies (E_0) of 10, 12.5, 15, 17.5, 20, 30, 50, and 100 eV over the scattering angle (θ) range of 5° to 130° in 5° intervals. However, comparison of our DCSs with those available in the literature (viz., Brunger and Teubner [5] and Cartwright *et al.* [6]) showed significant quantitative and qualitative differences between these measurements. In striking contrast, excellent qualitative agreement for all states was observed with DCSs taken by Zetner and Trajmar [7], and using a different instrument than [4], at the one E_0 value of 15 eV. Some important factors that can influence these differences in analyses of electron-energy-loss spectra have been discussed in [4], Campbell *et al.* [8], and Brunger and Buckman [9]:-

(i) The differences in Franck-Condon factors used. These vibrational wave-function overlap integrals [8] are computed

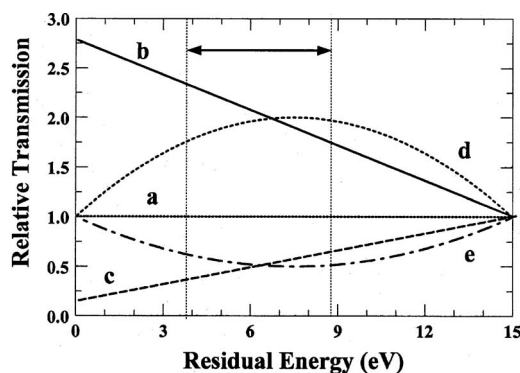


FIG. 1. Relative transmission functions used to modify electron-energy-loss spectra taken at $E_0=15$ eV. Transmission is set to 1 at the elastic scattering E_R of 15 eV. The spectral region of interest is indicated by the double-headed arrow (see text). (a) Flat. (b) Linearly decreasing function equal to 2 at the halfway E_R of 6.25 eV. (c) Linearly increasing function equal to 0.5 at the halfway E_R of 6.25 eV. (d) Parabolic convex function equal to 2 at $E_R=7.5$ eV and equal to 1 at E_R ends. (e) Parabolic concave transmission function equal to 0.5 at $E_R=7.5$ eV and equal to 1 at E_R ends.

from existing semiempirical potential energy curves and should include the effect of the electron moment as a function of the internuclear separation R . However, for potentials steep in R , e.g., for N_2 the electron moment is essentially constant and so its effect is neglected in the overlap integral.

(ii) The accurate determination of the transmission characteristics of the electron spectrometer used. This is generally calibrated against a helium energy-loss spectrum (see [4] or [5] and references therein).

(iii) The normalization of the intensities of the electronic features in the spectra to either elastic electron scattering or to available inelastic cross sections for the molecule, or both.

(iv) The determination of scattered electron backgrounds in these experiments especially for the elastic scattering peak.

(v) The effect of the base of the instrumental line profile (i.e., wings) in the spectra, which requires one to use more elaborate line profiles to unfold spectra as compared to the popular case of using single-Gaussian line profiles that do not model the wings of the energy-loss lines.

It has been suggested that the most likely factor influencing the differences between various measurements has been the transmission characteristic of the spectrometers employed. In this work, we have decided to focus solely on this transmission effect.

The present investigation uses the energy-loss spectra of [4] at $E_0=15$ eV where all past measurements are available. These spectra were taken using different calibration methods and more accurate background determinations recently available. At this energy, based on reliable time-of-flight data [10], we have determined the transmission of our spectrometer to be flat to within 8% [4]. Also, backgrounds in [4] were accurately determined using the movable source method recently developed in our laboratory [11]. Additionally, to unfold the molecular spectra in [4] we used a well-tested, visually interactive, multi-Gaussian line-profile least-squares fitting program [12]. Further, the electron

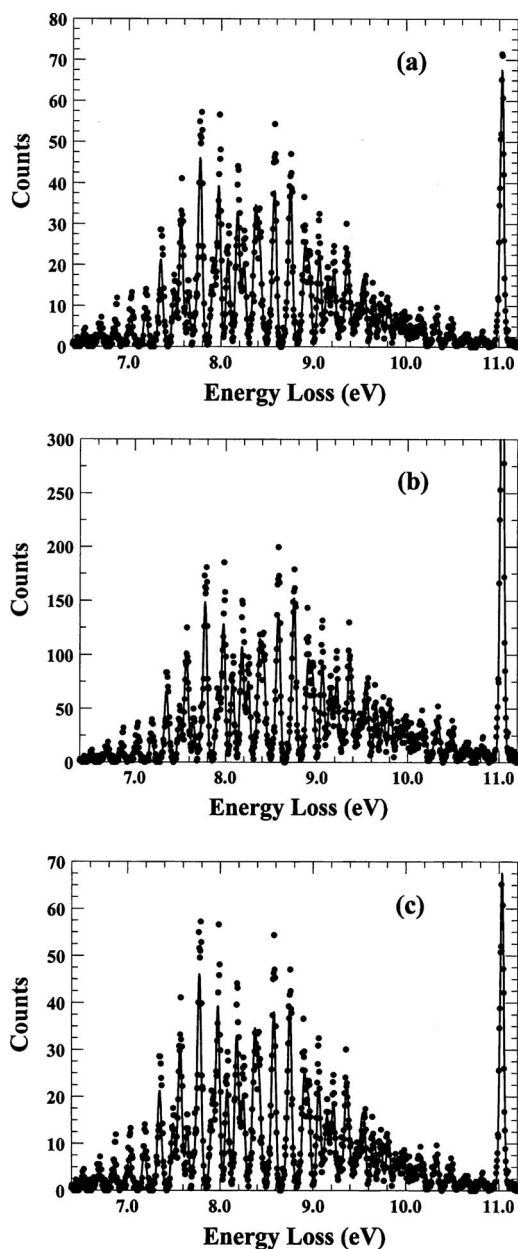


FIG. 2. Electron-energy-loss spectrum of N_2 taken at $E_0 = 15$ eV and $\theta=115^\circ$. The fits to these spectra (using flux-weighted Franck-Condon factors) are the solid lines in each graph. See text for details. (a) Transmission uncorrected spectrum (i.e., multiplied by transmission function a of Fig. 1). Fit reduced χ^2 is 1.5. (b) Same spectrum, but multiplied by linear transmission function b (see Fig. 1). Fit reduced χ^2 is 2.3. (c) Same spectrum, but multiplied by linear transmission function c (see Fig. 1). Fit reduced χ^2 is 2.7.

spectrometer used here has been extensively well-tested using rare-gas targets [12] and is thus expected to be reliable.

In this work, the energy-loss spectra taken in [4] were deliberately multiplied by several transmission curves described as functions of residual energy ($E_R=E_0-E_L$; where E_L is the energy loss). These transmission functions are detailed in Fig. 1.

The resultant spectra were unfolded (see Fig. 2) using the same Franck-Condon factors used in the analysis in [4], provided by Gilmore *et al.* [13], in excellent agreement with

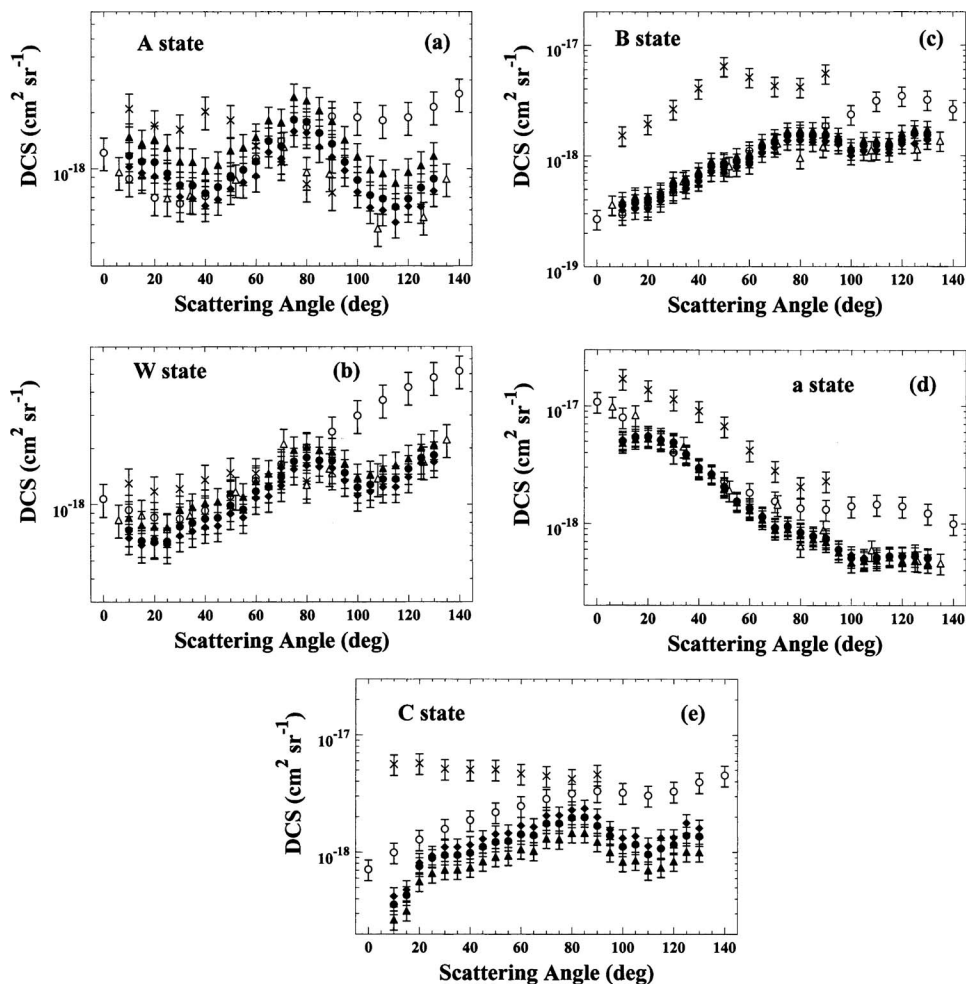


FIG. 3. DCSs for excitation of the various states (see graph) of N_2 at $E_0 = 15 \text{ eV}$. See text for further details. Present work: ● from original (uncorrected, i.e., multiplied by transmission function a) energy-loss spectra from [4], ▲ from the same spectra but multiplied by linear transmission function b, ◆ from the same spectra but multiplied by transmission function c (see Fig. 1). Previous experiments: × Brunger and Teubner [5]; ○ Cartwright *et al.* [6]; △ Zetner and Trajmar [7].

those of Trajmar [14]. After unfolding, the relative intensities of the energy-loss features corresponding to each electronic state were converted into DCSs by normalizing the total spectrum DCS to that established in the earlier DCSs in [4] for the complete spectrum. Note that at this incident energy flux-weighted Franck-Condon factors [4] were used.

A comparison of the DCSs obtained from spectra processed by transmission functions *a*, *b*, and *c* (Fig. 1) and then unfolded is presented for the dominant $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $a^1\Pi_g$, and $C^3\Pi_u$ states as shown in Fig. 3. Comparing with *a* (flat) we see that the effect of *b* is to decrease the $A^3\Sigma_u^+$, $B^3\Pi_g$, and $W^3\Delta_u$ DCSs while increasing the state $C^3\Pi_u$ DCS for this transmission function. The reverse is observed for *c*. The DCSs for the $a^1\Pi_g$ state are least affected for both *b* and *c*. The changes in the DCSs are smaller than one would intuitively expect, being typically $\approx 25\%$. This is significantly lower than differences between our DCSs and other DCSs which exceed a factor of 2. Functions *d* and *e* produce smaller changes than *b* and *c*, i.e., $\approx 18\%$. These are less effective at explaining differences among published DCSs.

The reduced size of these transmission effects can be understood by the extended energy range covered by a given electronic-vibrational manifold. Since this range is significantly larger than the width of an individual vibrational transition, the Franck-Condon unfolding method provides a reduced sensitivity to variations in transmission. As an

explanation of this conclusion, we look at the results of Zetner and Trajmar [7] which (when normalized to the same elastic DCSs as ours) are about a factor of ≈ 2 larger than our DCSs for all states ($A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, and $a^1\Pi_g$) determined by them [see Figs. 3(a)–3(d)]. A closer agreement with our DCSs is observed when the Zetner and Trajmar DCSs are multiplied by the factor 0.45 (see [4]). This indicates that their spectrometer had a likely transmission response similar to *b*, which quantitatively affected the inelastic DCSs more when they were normalized to the elastic DCSs (using the elastic peak) than from their unfolding analysis.

On the other hand, the DCSs of Cartwright *et al.* [6] are clearly in excellent quantitative agreement for the smaller θ for the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, and $a^1\Pi_g$ states, but deviate from ours at $\theta > 90^\circ$ [see Figs. 3(a)–3(d)]. In the case of the $C^3\Pi_u$ state [Fig. 3(e)], this disagreement is also quantitative at small θ , but the rise in their DCSs (compared to ours) for $\theta > 90^\circ$ is clearly seen here as well. This effect cannot be explained by transmission effects if their DCSs were taken contiguously with θ . A likely explanation for this disagreement is that their normalization to elastic scattering at $\theta > 90^\circ$ was a result of their use of a different instrument for scattering angles in this range. Since they normalized with similar elastic DCSs as all the other investigations, this provides a better explanation for the discrepancy with our measurements.

For the DCSs of Brunger and Teubner [5], we see good qualitative agreement with ours for the $B^3\Pi_g$, $W^3\Delta_u$, and $a^1\Pi_g$ states [Figs. 3(b)–3(d)], where their DCSs are about a factor of 2.5 above ours. Again this suggests the effect of their normalization to the elastic DCS, involving background in the elastic channel. However, this trend does not follow similarly for the $A^3\Sigma_u^+$ or the $C^3\Pi_u$ state [Figs. 3(a) and 3(e)], and cannot be explained solely by transmission effects involving normalization. As we have shown in the above analysis, the effect of transmission across the energy-loss spectrum is not a large enough effect to cover a discrepancy of over a factor of 4 for the $C^3\Pi_u$ state at small θ . Hence, some other instrumental effect must be partially responsible for the difference between their DCSs and ours. Hence, a separate investigation needs to be undertaken to gauge the difference between existing measurements.

Additionally, we carried out similar analysis of the spectra in [4] at $E_0=10$ and 12.5 eV, for a few selected spectra. Here, using the same transmissions we observed similar deviations of DCSs using transmission functions b and c as compared to the flat transmission function a . Again, transmission functions d and e did not exceed the variations for b and c .

The impact of transmission was also investigated for integral cross sections (ICSs) determined from the DCSs. Here, the transmission-affected DCSs were integrated into ICSs as described by Johnson *et al.* [15]. In most cases there was minimal difference between the ICSs at $E_0=15$ eV, with most transmission-modified ICSs falling within the stated 8% uncertainty of the flat-transmission ICSs. We note that the determination of the ICSs from the DCSs adds an uncertainty due to extrapolation of the DCSs to $\theta=0^\circ$ and to 180° .

We have shown that the effect of transmission of an electron spectrometer does not severely affect the unfolding of electronic vibrational manifolds using Franck-Condon factor

envelopes at intermediate energies (in this case at $E_0=15$ eV). In an effort to reconcile differences between other DCS data and ours, we report that other effects such as background evaluation and normalization to elastic scattering signal may be significant. Here, we cannot gauge the role of individual line profiles for other experiments. However, an investigation of electron scattering from molecular hydrogen [16,17] showed that wings in the line profiles appreciably affect the unfolding of nearby weaker transitions, if these wings are not properly modeled in the unfolding algorithms. Some reconciliation of past DCSs can be brought about from our analysis to provide more confidence in unfolding methods (as long as they are systematically carried out) and improve confidence in electron-molecule excitation DCSs. It is hoped that the present investigation will provide a collaborative impetus to experiment and theory to accurately probe the electron-impact differential scattering cross sections for these diatomic targets.

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