Intensities of infrared transitions in N_2O and H_2CO by electron impact spectroscopy

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Measurements of relative intensities of infrared transitions in N_2O and H_2CO have been made using forward inelastic scattering of 100 eV electrons. Agreement with previous infrared and electron impact measurements is satisfactory, showing that infrared intensities can be obtained from electron scattering measurements without the need for pressure broadening or corrections for the spectrometer slitwidth.

INTRODUCTION

The scattering of monoenergetic electron beams of high resolution ($\lesssim 0.020$ eV) in the energy range 200 eV to 35 keV has been used as a means of probing atomic and molecular energy levels.[1] Oscillator strengths in the far ultraviolet have been determined accurately in electron impact spectroscopy by assuming the validity of the Born approximation. In most cases there is excellent agreement with optical absorption measurements.

Recently, progress has been made using electron scattering measurements to determine absolute intensities in the infrared. Geiger and Wittmaack,[2] Skerbele *et al.*,[3] and Huebner *et al.*[4] have succeeded in resolving pure vibrational transitions in several molecules using electron spectrometers with extremely high energy resolution. This paper describes measurements of relative intensities of infrared transitions in N_2O and H_2CO using electron impact spectroscopy.

In a theoretical study of the stopping power of charged particles in matter, Bethe[5] was the first to show the close relationship between excitation by electron impact and absorption of radiation. This relationship was first exploited in experimental work by Lassettre and coworkers[1] on the electron impact excitation of atoms and molecules.

We consider inelastic collisions which take place between an incoming electron and an atom or molecule with excitations occurring to upper quantum states with E_n exceeding the energy E_0 of the ground state by ΔE_{0n}. If $\hbar\mathbf{k}_0, \hbar\mathbf{k}_f$ are the momentum vectors for the incident and scattered electrons, respectively, $\hbar\mathbf{K}$ is the momentum change vector, and θ is the angle between the incident and scattered electrons, then

$$K^2 = k_0^2 + k_f^2 - 2k_0k_f\cos\theta \; . \qquad (1)$$

If the energy of the incident electrons is much greater than ΔE_{0n} and the scattering angles are small, then the Born approximation can be used. In this approximation the differential cross section $d\sigma_{0n}/d\Omega$ for the excitation of a transition with momentum change $\hbar K$ is given by[1,5-8]

$$\frac{d\sigma_{0n}}{d\Omega} = \frac{4m^2e^4}{\hbar^4}\,\frac{k_f}{k_0K^4}\,|\epsilon_{0n}(K)|^2 \; , \qquad (2)$$

where $d\Omega$ is the differential solid angle,

$$|\epsilon_{0n}(K)|^2 = \left|\int \psi_0^*(\mathbf{r}_i)\left(\sum_{i=1}^{Z} e^{i\mathbf{K}\cdot\mathbf{r}_i}\right)\psi_n(\mathbf{r}_i)\,d\mathbf{r}_i\right|^2 \; , \qquad (3)$$

$\mathbf{r}_i$ is the position vector of the ith electron, ψ_0 and ψ_n are the wavefunctions for the ground and excited states, respectively, and $d\mathbf{r}_i$ is the volume element for all of the electrons in the atom or molecule. The summation is carried out over all Z atomic or molecular electrons.

It is useful[1,5-7] to define a quantity known as the generalized oscillator strength $f_{0n}(K)$, given by

$$f_{0n}(K) = (2m\Delta E_{0n}/\hbar^2K^2)\,|\epsilon_{0n}(K)|^2 \; . \qquad (4)$$

This depends only on the transition and on the momentum transfer $\hbar K$ and is thus independent of the incident electron energy. For small momentum transfer (high impact energy, small energy transfer, and/or small angle scattering), we can make the dipole approximation

$$e^{i\mathbf{K}\cdot\mathbf{r}_i} \cong 1 + i\mathbf{K}\cdot\mathbf{r}_i \; . \qquad (5)$$

Then

$$\begin{aligned}\epsilon_{0n}(K) &\cong Z\int \psi_0^*(\mathbf{r}_i)\psi_n(\mathbf{r}_i)\,d\mathbf{r}_i + i\mathbf{K}\cdot\int\psi_0^*(\mathbf{r}_i)\left(\sum_{i=1}^{Z}\mathbf{r}_i\right)\psi_n(\mathbf{r}_i)d\mathbf{r}_i \\ &= i\mathbf{K}\cdot\int\psi_0^*(\mathbf{r}_i)\left(\sum_{i=1}^{Z}\mathbf{r}_i\right)\psi_n(\mathbf{r}_i)d\mathbf{r}_i \; , \qquad (6)\end{aligned}$$

since ψ_0 and ψ_n are orthogonal. In order to compare with equations for optical absorption it is necessary to average $|\epsilon_{0n}(K)|^2$ over all orientations of the atom or molecule, or equivalently to average over all directions of $\mathbf{K}$. The result is[9]

$$\begin{aligned}|\epsilon_{0n}(K)|^2_{\mathrm{av}} &= \tfrac{1}{3}K^2\left|\int\psi_0^*(\mathbf{r}_i)\left(\sum_{i=1}^{Z}\mathbf{r}_i\right)\psi_n(\mathbf{r}_i)d\mathbf{r}_i\right|^2 \qquad (7) \\ &= \tfrac{1}{3}K^2|\mathbf{r}_{0n}|^2 \; ,\end{aligned}$$

where $|\mathbf{r}_{0n}|^2$ is the dipole matrix element. In this dipole approximation the generalized oscillator strength is independent of the momentum transfer, and is given by

$$f_{0n}(K) = (2m\Delta E_{0n}/3\hbar^2)\,|\mathbf{r}_{0n}|^2 \equiv f_{0n} \; , \qquad (8)$$

where f_{0n} is the optical oscillator strength.[7,10-12] Thus the generalized oscillator strength reduces to the optical oscillator strength in the limit of vanishing mo-

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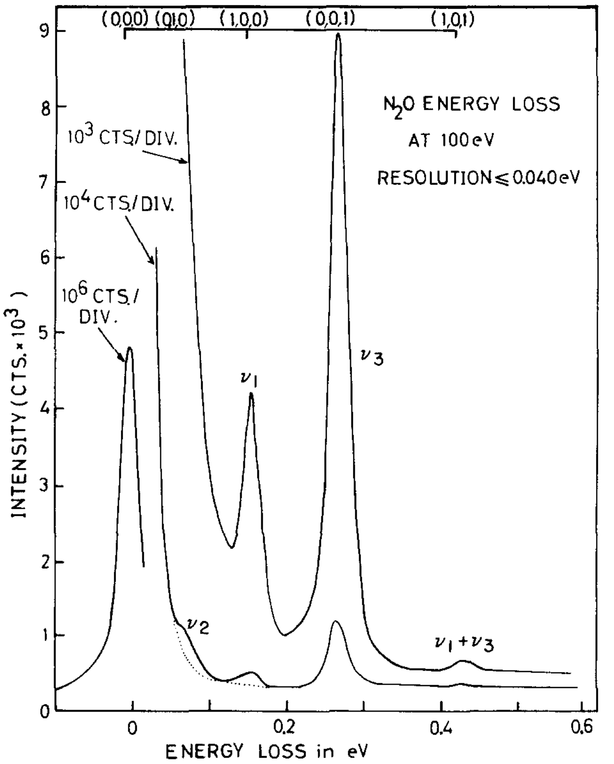

FIG. 1. Energy loss spectrum of nitrous oxide. The ν_2 fundamental appears as a shoulder on the unscattered peak indicated by the dotted line.

mentum transfer. This provides the basis for using small angle (hence small K) inelastic electron scattering to determine accurate optical oscillator strengths.[1,10–12]

In order to compare intensities measured in the infrared with those measured by electron scattering we need the relationship between the quantities measured by the two techniques.

In infrared measurements the quantity measured is the optical absorption coefficient k_ν integrated over all rotational components of a vibrational band and is given by[13–16]

$$\int k_\nu d\nu = \frac{2\pi e^2 E_{0n} N}{3\hbar^2 c} |\mathbf{r}_{0n}|^2 , \tag{9}$$

where N is the number density of absorbing molecules, ν is the frequency of the radiation, and we are assuming that hot bands are negligible. The integrated absorption coefficient is related to the optical oscillator strength by[13–16]

$$\int k_\nu d\nu = \frac{\pi e^2}{mc} N f_{0n} . \tag{10}$$

In electron scattering the quantity measured is the differential scattering cross section $d\sigma/d\Omega$ given by Eq. (2). To relate this to optical absorption, the dipole approximation of Eq. (7) is made:

$$\frac{d\sigma_{0n}}{d\Omega} = \frac{4m^2 e^4}{3\hbar^4} \frac{k_f}{k_0 K^2} |\mathbf{r}_{0n}|^2 . \tag{11}$$

Using Eq. (8) we obtain the relationship between the differential cross section and the optical oscillator strength:

$$\frac{d\sigma_{0n}}{d\Omega} = \frac{2me^4}{\hbar^2 \Delta E_{0n}} \frac{k_f}{k_0 K^2} f_{0n} \tag{12}$$

where, from Eq. (10), f_{0n} is proportional to the integrated optical absorption coefficient. It is convenient to introduce the atomic unit[17] of energy, $E_{at} = me^4/\hbar^2 = 27.212$ eV, so that

$$\frac{d\sigma_{0n}}{d\Omega} = 2 \frac{E_{at}}{\Delta E_{0n}} \frac{k_f}{k_0 K^2} f_{0n} . \tag{13}$$

For small energy losses and scattering angles, K^2 is given to a good approximation[10] by

$$K^2 = k_0 k_f [\theta^2 + (\Delta E_{0n}/2T)^2] , \tag{14}$$

where T is the kinetic energy of the incident electron. The observed cross section is obtained by integrating Eq. (13) from $\theta = 0$ to $\theta = \theta_{\max}$:

$$\sigma(\theta_{\max}) = \int_0^{\theta_{\max}} \frac{d\sigma}{d\Omega} d\Omega . \tag{15}$$

Using Eqs. (13) and (14) we find

$$\sigma(\theta_{\max}) = 2\pi \frac{E_{at}}{\Delta E_{0n}} \frac{1}{k_0^2} f_{0n} \ln\left[1 + \left(\frac{2T\theta_{\max}}{\Delta E_{0n}}\right)^2\right] . \tag{16}$$

It is worth noting that in employing the dipole approximation we are assuming that the generalized oscillator strength $f_{0n}(K)$ defined in Eq. (4) does not vary significantly over the small range of angles accepted by the electron spectrometer.

EXPERIMENTAL

The electron scattering apparatus used to study the pure vibrational spectrum of nitrous oxide and formaldehyde was operated with an incident electron beam energy of 100 eV for N_2O, 115 eV for H_2CO, a maximum scattering angle $\theta_{\max}$ of 0.02 rad, and a resolution of 0.030 eV (160 cm^{-1}). Details of the apparatus have been described in earlier publications.[4,18]

Nitrous oxide

Nitrous oxide was chosen for study because all three of its fundamental modes are infrared active and appear in both infrared absorption and electron impact spectra. The electron energy loss spectrum for N_2O is shown in Fig. 1. The fundamental modes ν_1 and ν_3 are completely resolved, while ν_2 appears as a shoulder on the steeply rising portion of the zero energy loss peak.

Peak areas were estimated by the method of counting squares. The ν_1 peak area was first determined relative to ν_3 (upper curve, Fig. 1), while ν_2 was measured relative to ν_1 (lower curve). The ν_2 peak area is subject to significant error because of the necessity of estimating the background intensity. This estimation is shown by the dotted curve in Fig. 1 and is based on the observation that the background, which is the tail of the no-loss beam, has a shape which is essentially independent of N_2O pressure. Geiger and Wittmaack[2] have also found that the background shape is independent of pressure. On this basis we estimate that the error

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TABLE I. Comparison of electron impact and infrared absorption data for N_2O.

			Relative intensities			
			Electron impact		Infrared absorption	
Symbol	Mode	ΔE(eV)	This work	Geiger and Wittmaack[a]	Eggers and Crawford[b]	Yamada and Person[c]
ν_1	Symmetric stretch	0.159	0.15	0.17	0.15	0.17
ν_2	Bending	0.073	0.05 ± 0.01	0.066	0.013	0.023
ν_3	Asymmetric stretch	0.276	1.00	1.00	1.00	1.00
$\nu_1 + \nu_3$	Combination	0.437	0.03	–	0.0015	–

[a] Reference 2. Values scaled using expression (17).

[b] Reference 20.

[c] Reference 21.

in the ν_2 peak area is less than about ±20%.

To compare these peak areas with the integrated infrared absorption coefficients (which are proportional to f_{0n}) we see from Eq. (16) that we must multiply the areas of the electron energy loss peaks by a scale factor

$$\Delta E_{0n}/\ln\left[1+\left(\frac{2T}{\Delta E_{0n}}\theta_{\max}\right)^2\right]. \qquad (17)$$

The scaled electron impact intensities of this work for N_2O, normalized[19] to the most intense peak from the ν_3 asymmetric stretch mode, are presented in Table I together with the scaled electron impact results of Geiger and Wittmaack[2] and the absolute infrared intensity measurements of Eggers and Crawford[20] and Yamada and Person.[21] Agreement between the four sets of values is good for ν_1, the symmetrical stretch mode, but the electron impact measurements give an intensity for the ν_2 mode which is higher than the intensity from infrared absorption by more than a factor of 2. It is possible that our result for the ν_2 peak area is too high because of an incorrect background subtraction. However, the ν_2 intensity obtained by Geiger and Wittmaack[2] is also substantially higher than that of Yamada and Person,[21] substantiating our conclusion that there may be some systematic reason for the difference. Possible reasons for this difference will be discussed below.

Results for H_2CO

Electron energy loss measurements for formaldehyde are shown in Fig. 2 for the energy loss range 0–0.6 eV. All six fundamentals are infrared active and are observed as partially resolved peaks in the energy loss spectrum. The unresolved peaks $\nu_4+\nu_6$, ν_2, and ν_3 were graphically deconvoluted in order to estimate their intensity, as shown by the dotted lines in Fig. 2. The scaled intensities are compared in Table II with the results of Hisatsune and Eggers,[22] who measured the absolute infrared intensities of the ν_2 and ν_3 fundamentals and the unresolved bands $\nu_1+\nu_5+2\nu_3$ and $\nu_4+\nu_6$. The notation used for the fundamentals is that of Mulliken.[23] The agreement between the two sets of results is within

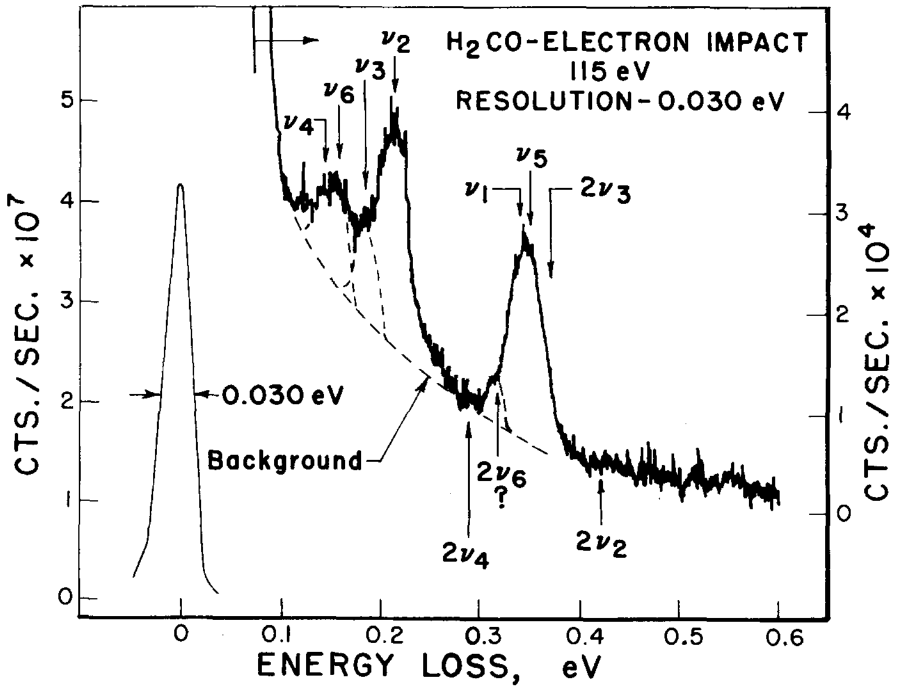

FIG. 2. Energy loss spectrum of formaldehyde. The arrows indicate the spectroscopic position of the peaks. No attempt was made to manually deconvolute the ν_4 and ν_6 fundamentals. The dotted line indicates the background due to the tail of the zero energy loss peak in the absence of any scattering gas.

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TABLE II. Comparison of electron impact and infrared absorption data for H_2CO.

			Relative intensities	
Symbol	Mode	ΔE(eV)	Electron impact[a]	Infrared absorption[b]
$\nu_1, \nu_5, 2\nu_3$	Unresolved triplet	0.360(AVE)	1.00	1.00
ν_2	H–C–H bending	0.215	0.7 ± 0.1	0.77
ν_4, ν_6	Unresolved doublet	0.152(AVE)	0.19 ± 0.04	0.13
ν_3	H–C–H scissors	0.186	0.20 ± 0.06	0.12

[a] This work.

[b] Hisatsune and Eggers, Ref. 22.

the combined experimental limits of uncertainty, taking into account the uncertainty in deconvoluting the unresolved peaks.

DISCUSSION

The generally good agreement between intensities obtained from electron impact and infrared absorption measurements shows that electron impact spectroscopy can be an important tool in determining relative, and perhaps absolute,[2,13] intensities of infrared transitions in molecules. There remains the question of the disagreement between electron impact and infrared absorption measurements of the ν_2 bending fundamental in N_2O. A similar, but larger, disagreement exists for the ratio of the ν_3 to the ν_2 transition in CO_2.[24]

It is possible that the disagreement arises from incorrect background subtraction in both electron scattering measurements, but this seems unlikely. There is also a possibility that the disagreement arises from the narrowness of the absorption lines making up a vibrational band. In electron impact spectroscopy, measurements of absolute line intensities are independent of the natural widths of the transitions, because each electron in the beam has an equal probability of being inelastically scattered with an energy loss ΔE_{0n} equal to the energy required to excite the transition. Hence the energy spread of the beam is merely convoluted with the natural width of the transition.[25] In ultraviolet absorption, however, serious differences exist between different measurements[26–28] when the spectrometer resolution is insufficient to completely resolve absorption features. The highly absorbing center of a narrow line absorbs the small fraction of the optical beam which lies near its center, while the bulk of the absorption comes from the wings of the line.[29] Hence the absorption coefficient will be underestimated unless special techniques are used.[29–31]

One of the techniques commonly used in infrared spectroscopy is to intentionally broaden spectral lines by introducing a foreign gas. Pressures of the foreign gas needed to adequately broaden the absorption line often exceed 10 atm. The assumption that the band strength is independent of pressure may be seriously in error for polar molecules.[32] The assumption that all the lines in a vibration–rotation band have the classical Lorenz shape and equal widths independent of rotational quantum number is clearly incorrect for HCl[33] and CO,[34] and probably for most molecules.[31] Noting that the measurements of Yamada and Person[21] depend on the assumption of equal line shapes and widths and were made at a relatively low broadening pressure (1 atm) and wide spectral band pass (2.1 cm^{-1}), together with the fact that N_2O is a polar molecule, it is perhaps not surprising that the infrared and electron impact measurements are in disagreement, particularly since it is well known[21] that the perpendicular vibrational bending mode for the linear triatomic molecules CS_2, CO_2, N_2O, and COS has an extremely sharp Q branch which contains a considerable fraction of the intensity.

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