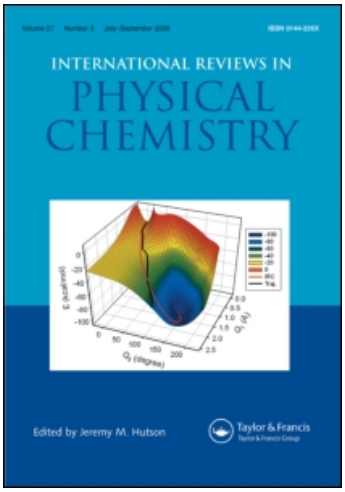
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Electron-impact vibrational excitation of polyatomic molecules

Yukikazu Itikawa

Online publication date: 26 November 2010

To cite this Article Itikawa, Yukikazu(1997) 'Electron-impact vibrational excitation of polyatomic molecules', International Reviews in Physical Chemistry, 16: 2, 155 — 176
To link to this Article: DOI: 10.1080/014423597230253
URL: http://dx.doi.org/10.1080/014423597230253

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1997, VOL. 16, NO. 2, 155–176

Electron-impact vibrational excitation of polyatomic molecules

by YUKIKAZU ITIKAWA

Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229, Japan

Vibrational excitation in electron collisions with polyatomic molecules is reviewed. Theoretical treatments based on the fixed-nuclear-orientation approximation are summarized. Results of the theoretical studies of H_2O, H_2S and CH_4 are presented as an example and compared with experimental data. A calculation in the Born approximation with a long-range electrostatic interaction is also shown. In particular, the usefulness of the Born approximation with a dipole interaction is examined in detail. Finally possible further improvement of the theory is discussed.

1. Introduction

In electron collisions with molecules, the excitation of molecular vibration is a very common process, unless the electron energy is very low. The vibrational excitation is the most important energy-loss process for an electron with energies less than a few tens of electron volts. In fact, vibrational excitation plays a critical role in the process of degradation or thermalization of high-energy (hot) electrons in a molecular gas (Kimura *et al.* 1993, Krajcar-Bronic and Kimura 1995). On the other hand the products of the process (i.e. the vibrationally excited molecules) are also of importance. Sometimes they are very active in reaction or other collision processes (Mason *et al.* 1994). They also affect electron transport in gases (Christophorou *et al.* 1991). The knowledge of electron-impact vibrational excitation therefore is needed in the fields of gaseous electronics, plasma chemistry, radiation science, planetary science and astrophysics.

Downloaded At: 17:04 21 January 2011

Vibration is a nuclear motion of a molecule. It is difficult for an electron to hit the nucleus directly to move it. The colliding electron first deforms the electron cloud in the molecule. Following the deformation, the nuclei change their positions to find a corresponding equilibrium configuration, thus leading to vibrational motion. In this sense, vibrational excitation occurs through a coupling of electronic and nuclear motions. This makes it difficult to formulate rigorously the process of vibrational excitation in general. Depending on the process considered, approximate methods have been proposed. Most of them, however, are concerned only with diatomic molecules. In the present paper, theoretical approaches are reviewed on the vibrational excitation of *polyatomic* molecules.

A polyatomic molecule has multiple modes of vibration. They have different fundamental frequencies and different symmetries. It is interesting to know how the excitation cross-section depends on the nature of the respective vibrational mode. Some of the vibrational transitions are infrared (IR) active. Do they matter in electron-impact excitation? Polyatomic molecules often have a vibrational mode with a very small excitation energy (say, less than 0·1 eV). Excitation of such a mode is energetically easy to achieve. It is of practical importance to know the magnitude of the cross-section for the excitation of such low-lying states. The dependence of the excitation cross-section on the collision energy and/or the scattering angle must reflect the details of the vibrational mode. This kind of systematic study of the vibrational excitation has not yet fully been attempted, because the problem is very complicated.

0144–235X/97 $12·00 © 1997 Taylor & Francis Ltd

Although a number of experimental results have been already reported, very few theoretical calculations have been performed on the vibrational excitation of polyatomic molecules (except for the somewhat extensive work on the resonance or the threshold structure in the cross-section of CO_2). A theoretical study is necessary to investigate the vibrational excitation in such a detailed manner as described above. Furthermore an experiment cannot give sufficient information about the cross-section. In the case of polyatomic molecules, different vibrational modes often have almost the same fundamental frequency. Excitation of these modes cannot be separated experimentally at least by the conventional technique. Another example is the angular dependence. A beam-type experiment cannot measure cross-sections at the angles near the forward ($\theta = 0^\circ$) and the backward ($\theta = 180^\circ$) directions. In these cases, experimental data have to be supplemented with theoretical information to give a complete picture of the vibrational excitation.

In the next section (section 2), general formulae are given for the calculation of the vibrational cross-section of polyatomic molecules. Emphasis is placed on the fixed-nuclear-orientation approximation. Section 3 describes the interaction between the colliding electron and the molecule taken in the cross-section calculation. Section 4 gives the cross-section formula in the Born approximation, which has been widely used in the analysis of experimental data. In section 5, examples of the calculation are presented for H_2O, H_2S and CH_4. Detailed comparisons are made between the theory and the experimental data available. Finally, in section 6, further improvement necessary in the theory is discussed.

A vibrational cross-section often shows structure ascribed to a resonance effect. Resonance phenomena in the electron–molecule collision have been discussed by many workers, although mostly for diatomic molecules. Recently Lucchese and Gianturco (1996) published a review article on the resonance in the case of polyatomic molecules. In the present paper, therefore, no specific attention is paid to the resonance effect in the vibrational cross-section.

Downloaded At: 17:04 21 January 2011

2. Theoretical method

2.1. *General formulae*

Theoretical methods for electron–molecule collisions have been reviewed many times (for the most recent review, see the book edited by Huo and Gianturco (1995)). Most of them deal with only diatomic molecules. When a polyatomic molecule is chosen as a target, the details of the formulation become much more complicated, although the essential part does not change. For an electron collision with polyatomic molecules, Gianturco and co-workers have published several review articles (Gianturco and Jain 1986, Gianturco 1995, Gianturco *et al.* 1995). In those articles, they mentioned vibrational excitations, but very briefly. In the present section, a theoretical method is shown in some more detail for the vibrational excitation of polyatomic molecules.

To solve the Schrödinger equation for a system of a colliding electron and a target molecule, we usually expand the total wavefunction in terms of the target eigenfunction. As a result we obtain a system of coupled equations for the wavefunction of the colliding electron (i.e. the so-called scattering equations). There are two different approaches to solve the scattering equations: firstly the close-coupling method and secondly the variational method. The first method is to solve the coupled equations with a truncation of channels to a finite number of closely coupled channels. It is straightforward but sometimes very time consuming. The second method is to apply

some kind of vibrational principle to the problem. In this case, instead of solving the scattering equations, one derives a scattering amplitude or scattering matrix from a variational formula. This method is rather easily applicable to a large molecule. To the knowledge of the present author, however, the variational method has seldom been applied to the calculation of the vibrational excitation of a polyatomic molecule. In the following, we present a theoretical formulation based on the close-coupling method. The essential ingredients of the theory are the same as those for diatomic molecules given in the paper, for example, by Morrison and Sun (1995). Atomic units are used throughout the present paper, unless otherwise noted.

First we consider the scattering problem in a space-fixed (SF) frame of coordinates. In this frame, the origin of the coordinate is fixed at the centre of gravity of the molecule and the z axis is taken along the direction of the incident electron. The wavefunction of the total (i.e. electron+molecule) system is expanded as

$$\Psi^{JM} = \sum_{n'l'j'\tau'} r^{-1} u^{JM}_{n'l'j'\tau'}(r)\, \chi_{n'}(\xi)\, \mathcal{Y}^{JM}_{l'j'\tau'}(\Omega, \hat{r}). \tag{2.1}$$

Here χ is the vibrational wavefunction of the target molecule. The normal coordinates and the vibrational quantum numbers are collectively denoted by ξ and n respectively (i.e. $\xi = (\xi_1, \xi_2, \dots)$ and $n = (n_1, n_2, \dots)$). The angular part of the wavefunction of the colliding electron (whose direction is denoted by $\hat{r}$) and the rotational wavefunction of the molecule (whose direction is denoted by the Euler angles Ω) are coupled to form an eigenfunction of the total angular momentum and its z component (J, M):

$$\mathcal{Y}^{JM}_{ljr}(\Omega, \hat{r}) = \sum_{m_j} \sum_{m_l} (j l m_j m_l | J M)\, \psi_{jm_j r}(\Omega)\, Y_{lm_l}(\hat{r}). \tag{2.2}$$

The quantum numbers (l, m_l) represent the magnitude of the orbital angular momentum of the colliding electron and its z component. The rotational angular momentum of the molecule and its z component are denoted by (j, m_j). The function ψ in equation (2.2) is an asymmetric-top wavefunction, which denotes the rotation of a polyatomic molecule. Its rotational state is designated by (j, m_j, τ). The quantity $(j l m_j m_l | J M)$ is the Clebsch–Gordan coefficient. It should be noted here that spin angular momentum is totally ignored in the present formulation. The target molecule is assumed to stay in its electronically ground state during the collision. An effect of the electronically excited state on the vibrational excitation has been seldom considered so far.

The Hamiltonian of the total system is

$$H = -\tfrac{1}{2}\nabla_r^2 + H_{\mathrm{mol}} + V, \tag{2.3}$$

where H_{mol} represents the Hamiltonian of the rotational and vibrational motion of the molecule and V is the interaction potential between the colliding electron and the molecule. We have to solve the Schrödinger equation

$$(H - E)\, \Psi^{JM} = 0. \tag{2.4}$$

After substituting equation (2.1) into equation (2.4), multiplying it on the left by the complex conjugate of the vibrational function and the angular basis function, and integrating that over the vibrational and angular variables, we obtain a set of coupled equations for the radial part of the wavefunction of the colliding electron in the form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l'(l'+1)}{r^2} + k^2_{n'j'\tau'}\right) u^{JM}_{n'l'j'\tau'}(r) = 2 \sum_{n''l''j''\tau''} \langle n'l'j'\tau' | V | n''l''j''\tau'' \rangle^{JM} u^{JM}_{n''l''j''\tau''}(r). \tag{2.5}$$

Downloaded At: 17:04 21 January 2011

The element of the interaction matrix is given by

$$\langle n'l'j'\tau'|V|n''l''j''\tau''\rangle^{JM} = \int \mathrm{d}\xi \int \mathrm{d}\Omega \int \mathrm{d}\hat{r}\,[\chi_{n'}(\xi)\,\mathscr{Y}^{JM}_{l'j'\tau'}(\Omega,\hat{r})]^* V\,[\chi_{n''}(\xi)\,\mathscr{Y}^{JM}_{l''j''\tau''}(\Omega,\hat{r})]. \tag{2.6}$$

The wavenumber k in equation (2.5) is defined by

$$k^2_{n'j'\tau'} = 2(E - E^{\mathrm{vib}}_{n'} - E^{\mathrm{rot}}_{j'\tau'}). \tag{2.7}$$

When an asymptotic form of the solution of the equations (2.5) is set to be as

$$u^{JM}_{n'l'j'\tau'}{}^{,nlj\tau}(r) \overset{r\to\infty}{\simeq} k^{-1/2}_{n'j'\tau'} \times \left\{\delta_{nn'}\delta_{ll'}\delta_{jj'}\delta_{\tau\tau'}\exp\left[-\mathrm{i}\left(k_{n'j'\tau'}r - \frac{\pi l'}{2}\right)\right] - S^{nlj\tau}_{n'l'j'\tau'}\exp\left[+\mathrm{i}\left(k_{n'j'\tau'}r - \frac{\pi l'}{2}\right)\right]\right\}, \tag{2.8}$$

then the scattering amplitude for the vibrational–rotational transition is obtained as

$$f_{n_0 j_0 \tau_0 m_{j_0}\to n'j'\tau' m_j}(\theta,\phi) = \left(\frac{\pi}{k_0 k_{n'j'\tau'}}\right)^{1/2} \sum_{JM}\sum_{ll'} \mathrm{i}^{l-l'+1}(2l+1)^{1/2}(j_0\, l\, m_{j_0}\, 0\,|\,J\,M) \times (\delta_{n_0 n'}\delta_{ll'}\delta_{j_0 j'}\delta_{\tau_0\tau'} - S^{n_0 l j_0 \tau_0}_{n'l'j'\tau'}) \sum_{m_l} (j'\, l'\, m_{j'}\, m_l\,|\,J\,M)\, Y_{l'm_l}(\theta,\phi). \tag{2.9}$$

The angles (θ, ϕ) denote the final direction of the scattered electron with respect to the incident electron. The differential cross-section (DCS) for the transition is calculated in the form

$$q(n_0 j_0\, \tau_0\, m_{j_0}\to n'j'\tau' m_{j'}) = \frac{k_{n'j'\tau'}}{k_0}\left|f_{n_0 j_0 \tau_0 m_{j_0}\to n'j'\tau' m_{j'}}(\theta,\phi)\right|^2. \tag{2.10}$$

Now we consider the same scattering problem in a molecule-fixed (MF) frame, where the coordinate origin is fixed at the gravity centre of the molecule and the z axis is chosen along one of the symmetry axes of the molecule. The SF and the MF frames are related through a conventional scheme of coordinate rotation. In particular, the spherical harmonics in the two frames satisfy the relation

$$Y_{lm_l}(\hat{r}) = \sum_{\mu_l} Y_{l\mu_l}(\hat{r}')\, D^{l}_{m_l\mu_l}{}^{*}(\Omega). \tag{2.11}$$

Here $\hat{r}'$ denotes the direction of the colliding electron in the MF frame, μ_l the z component of the orbital angular momentum in the MF frame, and D the Wigner rotation matrix.

In the MF frame, we introduce a symmetry-adapted angular basis function (Burke *et al.* 1972)

$$X^{\nu}_{l}(\hat{r}') = \sum_{\mu_l} b^{\nu}_{l\mu_l} Y_{l\mu_l}(\hat{r}'), \tag{2.12}$$

where the index ν denotes collectively the indices specifying the irreducible representation and those distinguishing the degenerated members. The explicit expressions of the coefficient b for the C_{2v} and O_h symmetries are given in the paper by Burke *et al.* (1972). Those for other symmetries can be constructed according to the formula

Downloaded At: 17:04 21 January 2011

given by, for example, Altman and Cracknell (1965). With use of the angular basis functions (2.12), the wavefunction of the total system is expressed in the MF frame as follows:

$$\Psi^{JM} = \sum_{n'l'v'\mu'} r^{-1} w^{JM}_{n'l'v'\mu'}(r)\, \chi_{n'}(\xi)\, \bar{D}^{J}_{M\mu'}{}^{*}(\Omega)\, X^{v'}_{l'}(\hat{r}'). \tag{2.13}$$

Here we have used a normalized D function (denoted by $\bar{D}$). The quantity μ is the MF-frame z component of the total angular momentum of the system. After inserting equation (2.13) into equation (2.4) and taking the same procedure as in the SF frame, we have the scattering equations in the form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l'(l'+1)}{r^2} + k^2_{n'}\right) w^{JM}_{n'l'v'\mu'}(r) = 2 \sum_{n''l''v''\mu''} \langle n'l'v'\mu' | V | n''l''v''\mu'' \rangle^{JM} w^{JM}_{n''l''v''\mu''}(r) + 2 \sum_{n''v''\mu''} \langle n'v'\mu' | H_{\mathrm{rot}} | n''v''\mu'' \rangle^{JMl'} w^{JM}_{n''l'v''\mu''}(r). \tag{2.14}$$

The element of the interaction matrix is obtained as

$$\langle n'l'v'\mu' | V | n''l''v''\mu'' \rangle^{JM} = \delta_{\mu'\mu''} \langle n'l'v' | V | n''l''v'' \rangle, \tag{2.15}$$

with

$$\langle n'l'v' | V | n''l''v'' \rangle = \int \mathrm{d}\xi \int \mathrm{d}\hat{r}' [\chi_{n'}(\xi)\, X^{v'}_{l'}(\hat{r}')]^{*} V [\chi_{n''}(\xi)\, X^{v''}_{l''}(\hat{r}')]. \tag{2.16}$$

The interaction matrix element in this case does not depend on μ, because the electron–molecule interaction depends only on the position of the colliding electron relative to the molecule and not on the molecular orientation in the space. The second term on the right-hand side of equation (2.14) appears owing to the rotation of the coordinates.

To obtain the scattering amplitude, we have to go back to the SF frame. Comparing the two expansion forms (2.1) and (2.13) and using the equation (2.11), we obtain a formula for the frame transformation in the form

$$w^{JM}_{n'l'v'\mu'} = \sum_{j'\tau'} B_{j'\tau',v'\mu'}(Jl')\, u^{JM}_{n'l'j'\tau'}, \tag{2.17}$$

with the transformation coefficient

$$B_{j'\tau',v'\mu'}(Jl') = \sum_{\mu_l} a^{j'}_{\tau',\mu'-\mu_l} b^{v'}_{l'\mu_l}{}^{*} \left(\frac{2j'+1}{2J+1}\right)^{1/2} (j'l'\mu' - \mu_l\, \mu_l\, | J\mu'). \tag{2.18}$$

The transformation is unitary so that we also have

$$u^{JM}_{n'l'j'\tau'} = \sum_{v'\mu'} B^{*}_{j'\tau',v'\mu'}(Jl')\, w^{JM}_{n'l'v'\mu'}. \tag{2.19}$$

On the right-hand side of equation (2.18), b is the coefficient appearing in equation (2.12) and a is the expansion coefficient of the asymmetric-top function in terms of the D function as

$$\psi_{jm_j\tau}(\Omega) = \sum_{\mu_j} a^{j}_{\tau\mu_j} \bar{D}^{j}_{m_j\mu_j}{}^{*}(\Omega). \tag{2.20}$$

2.2. *Fixed-nuclear-orientation approximation*

Usually the molecular rotation is very slow compared with the speed of the incident electron. We can safely assume that the molecular orientation does not change during the collision. This is called the fixed-nuclear-orientation (FNO) approximation or the

Downloaded At: 17:04 21 January 2011

rotationally sudden approximation. In the MF frame, this approximation corresponds to the neglect of the second term on the right-hand side of equation (2.14). Thus the scattering equation in the FNO approximation are obtained in the form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l'(l'+1)}{r^2}+k_{n'}^2\right)w_{n'l'\nu'\mu'}(r) = 2\sum_{n''l''\nu''}\langle n'l'\nu'|V|n''l''\nu''\rangle w_{n''l''\nu''\mu'}(r). \tag{2.21}$$

In this approximation, μ is conserved during the collision. We drop the index μ of the radial function w hereafter. We solve equation (2.21) with an asymptotic condition

$$w_{n'l'\nu'}^{nl\nu}(r) \overset{r\to\infty}{\simeq} k_{n'}^{-1/2}\left\{\delta_{nn'}\delta_{ll'}\delta_{\nu\nu'}\exp\left[-\mathrm{i}\left(k_{n'}r-\frac{\pi l'}{2}\right)\right]-S_{n'l'\nu'}^{nl\nu}\exp\left[+\mathrm{i}\left(k_{n'}r-\frac{\pi l'}{2}\right)\right]\right\} \tag{2.22}$$

and obtain the **S** matrix in the MF frame. Through the frame transformation (2.19), the **S** matrix in the SF frame is calculated as

$$S_{n'l'j'\tau'}^{nlj\tau} = \sum_{\mu}\sum_{\nu\nu'} B_{j\tau,\nu\mu}(Jl)\,B^{*}_{j'\tau',\nu'\mu}(Jl')\,S_{n'l'\nu'}^{nl\nu}. \tag{2.23}$$

Inserting this **S** matrix into (2.9), we can obtain the scattering amplitude and therefrom the DCS for the vibrational–rotational transition.

In the present paper, we are concerned only with the vibrational transition and take an average over the initial rotational states and a sum over the final rotational states of the cross section. Then the DCS for the vibrational transition $n_0 \to n'$ is obtained as

$$q^{\mathrm{FNO}}(n_0\to n') = \sum_{L} A_L P_L(\cos\theta), \tag{2.24}$$

with the coefficient

$$\begin{aligned} A_L = {} & \frac{1}{4k_0^2}(2L+1)\sum_{l\bar{l}}\sum_{l'\bar{l}'}\sum_{\nu\bar{\nu}}\sum_{\nu'\bar{\nu}'}\sum_{\mu_l\bar{\mu}_l}\sum_{\mu_{l'}\bar{\mu}_{l'}}\mathrm{i}^{L-l'-\bar{l}+\bar{l}'}[(2l+1)(2\bar{l}+1)(2l'+1)(2\bar{l}'+1)]^{1/2} \\ & \times(-1)^{\mu_{l'}+\mu_l}\begin{pmatrix} l & \bar{l} & L \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & \bar{l}' & L \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & \bar{l} & L \\ \mu_l & -\bar{\mu}_l & m_L\end{pmatrix}\begin{pmatrix} l' & \bar{l}' & L \\ \mu_{l'} & -\bar{\mu}_{l'} & m_L\end{pmatrix} \\ & \times(b_{l'\mu_{l'}}^{\nu'}S_{n'l'\nu'}^{n_0 l\nu}b_{l\mu_l}^{\nu}{}^{*})(b_{l'\bar{\mu}_{l'}}^{\bar{\nu}'}S_{n'\bar{l}'\bar{\nu}'}^{n_0\bar{l}\bar{\nu}}b_{l\bar{\mu}_l}^{\bar{\nu}}{}^{*})^{*}. \end{aligned} \tag{2.25}$$

The corresponding formula for the integral cross-section (ICS) is

$$Q^{\mathrm{FNO}}(n_0\to n') = \frac{\pi}{k_0^2}\sum_{ll'}\sum_{\nu\nu'}|S_{n'l'\nu'}^{n_0 l\nu}|^2. \tag{2.26}$$

In equations (2.24) and (2.25), P_L is the Legendre function of order L and $\begin{pmatrix} l & \bar{l} & L \\ 0 & 0 & 0\end{pmatrix}$, etc., are the $3-j$ symbols.

2.3. *Vibrationally sudden approximation*

To solve the scattering equations in the FNO approximation (2.21), a further simplification is often made. If the collision is fast compared with the molecular vibration, we can ignore the vibrational excitation energy compared with the kinetic energy of the incident electron. That is, we can assume that $k_n = k$. Then equation (2.21) becomes

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l'(l'+1)}{r^2}+k^2\right)w_{n'l'\nu'}(r) = 2\sum_{n''l''\nu''}\langle n'l'\nu'|V|n''l''\nu''\rangle w_{n''l''\nu''}(r). \tag{2.27}$$

Downloaded At: 17:04 21 January 2011

A solution of this equation can be obtained in the following way. First we solve

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{l'(l'+1)}{r^2}+k^2\right)\tilde{w}_{l'v'}(r;\xi) = 2\sum_{l''v''}\langle l'v'|V|l''v''\rangle\,\tilde{w}_{l''v''}(r;\xi) \tag{2.28}$$

at a fixed nuclear configuration designated by ξ. Then the solution of equation (2.27) is constructed as

$$w^{nlv}_{n'l'v'}(r) = \int \mathrm{d}\xi\,\chi^*_n(\xi)\,\tilde{w}^{lv}_{l'v'}(r;\xi)\,\chi_n(\xi). \tag{2.29}$$

The element of the interaction matrix in equation (2.28) is given by

$$\langle l'v'|V|l''v''\rangle = \int \mathrm{d}\hat{r}'\,X^{v'}_{l'}{}^*(\hat{r}')\,VX^{v''}_{l''}(\hat{r}'). \tag{2.30}$$

When we solve equation (2.28) with an asymptotic condition

$$\tilde{w}^{lv}_{l'v'}(r;\xi) \overset{r\to\infty}{\simeq} k^{-1/2}\left\{\delta_{ll'}\delta_{vv'}\exp\left[-\mathrm{i}\left(kr-\frac{\pi l'}{2}\right)\right]-\tilde{S}^{lv}_{l'v'}(\xi)\exp\left[+\mathrm{i}\left(kr-\frac{\pi l'}{2}\right)\right]\right\}, \tag{2.31}$$

the **S** matrix in the MF frame is obtained as

$$S^{nlv}_{n'l'v'} = \int \mathrm{d}\xi\,\chi^*_n(\xi)\,\tilde{S}^{lv}_{l'v'}(\xi)\,\chi_n(\xi). \tag{2.32}$$

The scheme of approximation described here is called the vibrationally sudden approximation or sometimes the adiabatic-nuclei approximation. The scattering equations (2.28) are rather simple to solve, but they have to be solved at many different positions of nuclei. The disadvantage of the method is its inapplicability near threshold, where the collision energy is comparable with the excitation energy. There have been several proposals to correct this deficiency (for example, Morrison and Sun (1995)).

Downloaded At: 17:04 21 January 2011

3. Interaction between the colliding electron and the target molecule

The main part of the interaction is the electrostatic contribution V^{st}. It is composed of two parts: the Coulomb interaction V^{el} of the colliding electron with the molecule electrons and the interaction V^{nuc} with the nuclei. That is

$$V^{\mathrm{st}}(\mathbf{r},\xi) = V^{\mathrm{el}}(\mathbf{r},\xi)+V^{\mathrm{nuc}}(\mathbf{r},\xi), \tag{3.1}$$

$$V^{\mathrm{el}} = \int \mathrm{d}\mathbf{r}_i\,\rho^{\mathrm{el}}(\mathbf{r}_i,\xi)\frac{1}{|\mathbf{r}-\mathbf{r}_i|}, \tag{3.2}$$

$$V^{\mathrm{nuc}} = -\sum_{j=1}^{N}\frac{Z_j}{|\mathbf{r}-\mathbf{R}_j|}. \tag{3.3}$$

Here ρ^{el} denotes the density of the molecular electrons (whose position is denoted by $\mathbf{r}_i$) and $\mathbf{R}_j$ the position of the jth nucleus with charge Z_j. It should be noted that all the interaction potentials depend on the nuclear configuration, which is specified by the normal coordinate ξ. Now we consider the interaction matrix in the MF frame (2.16). To evaluate this, we expand the potential in terms of the symmetry-adapted angular basis function (2.12):

$$V^{\mathrm{st}}(\mathbf{r},\xi) = \sum_{\lambda\eta} V^{\mathrm{st}}_{\lambda\eta}(r,\xi)\,X^{\eta}_{\lambda}(\hat{r}). \tag{3.4}$$

In this section, everything is referred to the MF frame, so that $\hat{r}$ is used instead of $\hat{r}'$ in equation (2.12). Substituting equation (3.4) into equation (2.16), we have

$$\langle n'l'v'|V^{\mathrm{st}}|n''l''v''\rangle = \sum_{\lambda\eta}\langle n'|V^{\mathrm{st}}_{\lambda\eta}|n''\rangle X\begin{bmatrix} l' & \lambda & l'' \\ v' & \eta & v'' \end{bmatrix}. \tag{3.5}$$

Here we have separated the integral into the angular part

$$X\begin{bmatrix} l' & \lambda & l'' \\ v' & \eta & v'' \end{bmatrix} = \int \mathrm{d}\hat{r}\, X^{v'}_{l'} * X^{\eta}_{\lambda} X^{v''}_{l''} \tag{3.6}$$

and the vibrational part

$$\langle n'|V^{\mathrm{st}}_{\lambda\eta}|n''\rangle = \int \mathrm{d}\xi\, \chi^{*}_{n'}(\xi)\, V^{\mathrm{st}}_{\lambda\eta}(r,\xi)\, \chi_{n''}(\xi). \tag{3.7}$$

The angular integral (3.6) can be calculated analytically. To calculate the integral (3.7) we need an explicit form of the molecular vibrational function.

Now a simple method to evaluate equation (3.7) is introduced. First we assume the vibration to be harmonic. Then we expand the potential in terms of the normal coordinates around the equilibrium position to the first order:

$$V^{\mathrm{st}}_{\lambda\eta}(r,\xi) = V^{\mathrm{st}}_{\lambda\eta}(r,\xi=0) + \sum_s \left(\frac{\partial V^{\mathrm{st}}_{\lambda\eta}}{\partial \xi_s}\right)_{\xi=0} \xi_s. \tag{3.8}$$

Finally we obtain the relevant element of the matrix in the form

$$\langle n'|V^{\mathrm{st}}_{\lambda\eta}|n''\rangle = V^{\mathrm{st}}_{\lambda\eta}(r,\xi=0)\,\delta_{n'n''} + \sum_s \left(\frac{\partial V^{\mathrm{st}}_{\lambda\eta}}{\partial \xi_s}\right)_{\xi=0} \langle n'|\xi_s|n''\rangle, \tag{3.9}$$

with

$$\langle n'|\xi_s|n''\rangle = \left[\left(\frac{n'_s+1}{2}\right)^{1/2}\delta_{n''_s,\,n'_s+1} + \left(\frac{n'_s}{2}\right)^{1/2}\delta_{n''_s,\,n'_s-1}\right]\prod_{p(\neq s)}\delta_{n'_p n''_p}. \tag{3.10}$$

In this method we need no explicit form of the vibrational wavefunction. Furthermore we do not need to calculate the potential at any other nuclear configuration than the equilibrium configuration. Additional information that we need is the normal-coordinate derivative of the potential at the equilibrium position. The form (3.9) can reliably be used at least when we consider lower vibrational states.

One of the features of the electron–molecule collision distinguished from the electron–atom collision is the presence of a long-range interaction in the former. The long-range interaction arises from an electronic multipole moment of the molecule. Using the multipole expansion

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{\lambda}\frac{r_2^{\lambda}}{r_1^{\lambda+1}}\frac{4\pi}{2\lambda+1}\sum_{\nu} X^{\nu}_{\lambda}{}^{*}(\hat{r}_1)\, X^{\nu}_{\lambda}(\hat{r}_2) \quad \text{for } r_1 > r_2. \tag{3.11}$$

The electrostatic potential is reduced to its long-range part. That is, when the colliding electron is located far apart from the target molecule,

$$V^{\mathrm{st}} \to V^{\mathrm{st}}_{\mathrm{LR}} = \sum_{\lambda\eta} V^{\mathrm{LR}}_{\lambda\eta}(r,\xi)\, X^{\eta}_{\lambda}(\hat{r}), \tag{3.12}$$

with

$$V^{\mathrm{LR}}_{\lambda\eta}(r,\xi) = -\left(\frac{4\pi}{2\lambda+1}\right)^{1/2} M^{(\lambda)}_{\eta}(\xi) r^{-\lambda-1}. \tag{3.13}$$

Downloaded At: 17:04 21 January 2011

The quantity $M_\eta^{(\lambda)}$ is the electric multipole moment defined by

$$M_\eta^{(\lambda)}(\xi) = \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} \int \mathrm{d}\mathbf{r}_i \rho(\mathbf{r}_i, \xi)\, r_i^{\lambda} X_\lambda^{\eta *}(\hat{r}_i). \tag{3.14}$$

In other words, $M_\eta^{(\lambda)}$ with $\lambda = 1, 2, \ldots$ are the dipole, quadrupole,..., moments respectively of the molecule. In equation (3.14), ρ is the charge density of the molecule, including both the electronic and the nuclear contributions. Thus the vibrational matrix element of the multipole moment or the derivative of the multipole moment is an important quantity in causing a vibrational transition.

When we consider the electrostatic potential of a molecule, the molecule is assumed not to be deformed by the incoming electron. By this assumption, we implicitly distinguish the colliding and the molecular electrons. Quantum-mechanically the total wavefunction should be antisymmetric with respect to the interchange of any two of the incident plus molecular electrons. This gives rise to an exchange effect of electrons. This effect can be treated rigorously, if we properly antisymmetrize the total wavefunction (for example Gianturco *et al.* (1995)). The resulting scattering equations, however, include non-local terms, thereby becoming much more difficult to solve. To circumvent this difficulty, various kinds of local model potential have been proposed to take into account this exchange effect effectively. Here we show one example: the free-electron-gas exchange model potential proposed by Hara (1967), which is given by

$$V^{\mathrm{ex}}(\mathbf{r}, \xi) = -\frac{2}{\pi} k_{\mathrm{F}} \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|\right), \tag{3.15}$$

with

$$\eta(\mathbf{r}, \xi) = \frac{(k^2 + 2I + k_{\mathrm{F}}^2)^{1/2}}{k_{\mathrm{F}}}, \tag{3.16}$$

$$k_{\mathrm{F}}(\mathbf{r}, \xi) = [3\pi^2 \rho^{\mathrm{el}}(\mathbf{r}, \xi)]^{1/3}. \tag{3.17}$$

In this model, the molecular electrons are treated as a free-electron gas with the density ρ^{el} and the incident electron is assumed as a plane wave. The quantity I in equation (3.16) is the ionization potential of the molecule. The accuracy of this and other model exchange potentials have been examined in many cases (for example, Gianturco *et al.* (1995)).

In the actual collision process, the target molecule is distorted by the incoming electron. Strictly speaking, this distortion (the so-called target polarization) depends on the speed of the incident electron. Quantum-mechanically it can be interpreted as a virtual excitation of the energetically inaccessible electronic states of the target. Any rigorous treatment of this effect is very difficult and still remains to be one of the greatest problems in the theory of electron collision with atoms and molecules. A number of approximate methods have been proposed to include effectively the target polarization in the collision calculation. A simple way is to introduce a local model potential also for this effect. One of the model potential is the correlation–polarization potential defined by (Padial and Norcross 1984)

$$\begin{aligned} V^{\mathrm{pol}}(\mathbf{r}, \xi) &= V_{\mathrm{LR}}^{\mathrm{pol}}(\mathbf{r}, \xi), \quad \text{for } r > r_{\mathrm{c}}, \\ &= V^{\mathrm{corr}}(\mathbf{r}, \xi), \quad \text{for } r < r_{\mathrm{c}}. \end{aligned} \tag{3.18}$$

Here the long-range part is given by the asymptotic polarization potential in the form

$$V_{\mathrm{LR}}^{\mathrm{pol}} = -\frac{1}{2r^4}[\alpha_{xx}(\hat{r}\cdot\hat{x})^2 + \alpha_{yy}(\hat{r}\cdot\hat{y})^2 + \alpha_{zz}(\hat{r}\cdot\hat{z})^2], \tag{3.19}$$

Downloaded At: 17:04 21 January 2011

with a molecular polarizability tensor α_{ij}. The short-range part in equation (3.18) is the correlation potential calculated by the local-density approximation of electron gas. The short- and long-range parts are matched at the crossing point (r_c) of the two parts as a function of electron distance r. This model polarization potential has been successfully applied to many collision systems. This and some other methods to consider the target polarization have been discussed by Gianturco *et al.* (1995).

When we consider the effects of electron exchange and target polarization with local model potentials V^{ex} and V^{pol} respectively, the static potential V^{st} in equations (3.4)–(3.9) should be replaced by the sum $V = V^{st} + V^{ex} + V^{pol}$. In some cases the asymptotic part of the polarization (3.19) is also important as a long-range interaction such as V^{st}_{LR}.

4. The Born approximation for vibrational transitions

A simple method of cross-section calculation is an application of the perturbation theory. If the terms on the right-hand side of equation (2.21) are small, the equation can be solved in the Born approximation. The first-order solution gives the **S** matrix in the form

$$(S^{nl\nu}_{n'l'\nu'})^{Born} = -4i(k_n k_{n'})^{1/2} \int_0^\infty dr\, r^2 j_l(k_n r) j_{l'}(k_{n'} r) \langle n'l'\nu' | V | nl\nu \rangle, \tag{4.1}$$

where j_l is the spherical Bessel function of lth order. When we put this into equations (2.25) and (2.26), we obtain the relevant cross-section in the (first-order) Born approximation. Over 20 years ago, Itikawa (1974) derived a general Born formula for the vibrational excitation cross-section of a polyatomic molecule without resorting to the partial wave expansion. As is shown in section 3, the interaction potential is expanded in terms of the symmetry-adapted angular basis function as

$$V(\mathbf{r}, \xi) = \sum_{\lambda\eta} V_{\lambda\eta}(r, \xi) X^{\eta}_{\lambda}(\hat{r}). \tag{4.2}$$

(In the 1974 paper of Itikawa, the function $Z_{lm\delta}$ is used instead of X^{η}_{λ}, but these two have essentially the same meaning.) On the basis of the standard theory of perturbation, Itikawa derived the DCS for the vibrational transition as follows:

$$q^{Born}(n_0 \to n') = \frac{1}{\pi} \frac{k_{n'}}{k_0} \sum_{\lambda\eta} \left| \int_0^\infty dr\, r^2 j_\lambda(Kr) \langle n' | V_{\lambda\eta} | n_0 \rangle \right|^2. \tag{4.3}$$

Here K is the momentum transferred and given by

$$K^2 = k_0^2 + k_{n'}^2 - 2k_0 k_{n'} \cos\theta. \tag{4.4}$$

Using this relation, the ICS can be calculated from

$$Q^{Born}(n_0 \to n') = \frac{2\pi}{k_0 k_{n'}} \int_{|k_0 - k_{n'}|}^{k_0 + k_{n'}} q^{Born}(n_0 \to n') K\, dK. \tag{4.5}$$

Now we consider only the long-range electrostatic interaction. The Born method is best reliable when those long-range forces dominate the collision process. When the colliding electron is far from the molecule, the electrostatic interaction is reduced to its long-range part (see equation (3.12))

$$V_{\lambda\eta} \to -\left(\frac{4\pi}{2\lambda+1}\right)^{1/2} M^{(\lambda)}_{\eta}(\xi) \frac{1}{r^{\lambda+1}}. \tag{4.6}$$

Downloaded At: 17:04 21 January 2011

Substituting this into equation (4.3), we have

$$q^{\text{Born, LR}}(n_0 \to n') = \frac{1}{\pi}\frac{k_{n'}}{k_0}\sum_{\lambda\eta}\frac{4\pi}{2\lambda+1}\left|\langle n'\left|M_\eta^{(\lambda)}\right|n_0\rangle\right|^2\left|\int_0^\infty \mathrm{d}r\, r^2 j_\lambda(Kr)\, r^{-\lambda-1}\right|^2. \tag{4.7}$$

Using the formula

$$\int_0^\infty \mathrm{d}r\, r^2 j_\lambda(Kr) r^{-\lambda-1} = \frac{1}{(2\lambda-1)!!}K^{\lambda-2}, \tag{4.8}$$

we finally obtain

$$q^{\text{Born, LR}}(n_0 \to n') = 4\frac{k_{n'}}{k_0}\sum_{\lambda\eta}\frac{1}{2\lambda+1}\left(\frac{1}{(2\lambda-1)!!}K^{\lambda-2}\right)^2\left|\langle n'\left|M_\eta^{(\lambda)}\right|n_0\rangle\right|^2. \tag{4.9}$$

In particular a dipole interaction gives

$$q^{\text{Born, dipole}}(n_0 \to n') = \frac{4}{3}\frac{k_{n'}}{k_0}\frac{1}{K^2}\sum_\eta\left|\langle n'\left|M_\eta^{(1)}\right|n_0\rangle\right|^2, \tag{4.10}$$

$$Q^{\text{Born, dipole}}(n_0 \to n') = \frac{8\pi}{3}\frac{1}{k_0^2}\ln\left|\frac{k_0+k_{n'}}{k_0-k_{n'}}\right|\sum_\eta\left|\langle n'\left|M_\eta^{(1)}\right|n_0\rangle\right|^2. \tag{4.11}$$

Downloaded At: 17:04 21 January 2011

The dipole matrix element $\langle n'|M_\eta^{(1)}|n_0\rangle$ is the quantity describing the extent of emission or absorption of IR light by a molecule. In fact the IR absorption intensity A is given by the formula

$$A(n' \leftarrow n_0) = \frac{2\pi\omega}{3\hbar c}\sum_\eta\left|\langle n'\left|M_\eta^{(1)}\right|n_0\rangle\right|^2, \tag{4.12}$$

where ω is the corresponding IR frequency. Thus, once we know the relevant IR intensity, we can immediately calculate the vibrational cross-section approximately as in equations (4.10) and (4.11). Although already well known for diatomic molecules, this was applied to polyatomic molecules for the first time by Itikawa (1971) for CO_2 and by Davis and Schmidt (1972) for CH_4 and other hydrocarbons. Since then this relation has been widely used by experimentalists to compare with their cross-section data.

Figure 1 shows one example of comparison of the experimental data with the Born cross-section. The figure compares the DCS for the vibrational excitation of CF_3Cl experimentally obtained by Mann and Linder (1992), with the corresponding Born value calculated with a dipole interaction (called the Born dipole cross-section, hereafter). The molecule CF_3Cl has six normal modes of vibration, of which ν_1, ν_2, ν_4 and ν_5 are IR active. The excitation of ν_1 and ν_4 cannot be separated experimentally so that the sum of the respective cross-sections is shown in the figure (as $\nu_{1,4}$). The Born dipole approximation reproduces very well the experimental data for the $\nu_{1,4}$ mode, particularly at the lowest energy considered. For other IR-active modes (i.e. ν_2 and ν_5), the Born dipole theory does not work well, except in the region of small scattering angles where no experimental data are available.

As is seen from the formula above, the Born dipole cross-section is proportional to the dipole matrix element squared. That quantity can be derived from the IR intensity A and the vibrational frequency ω as

$$\sum_\eta\left|\langle n'\left|M_\eta^{(1)}\right|n_0\rangle\right|^2(\text{au}) = 0{\cdot}061\,757\frac{A\,(\text{km mol}^{-1})}{\omega\,(\text{cm}^{-1})}. \tag{4.13}$$

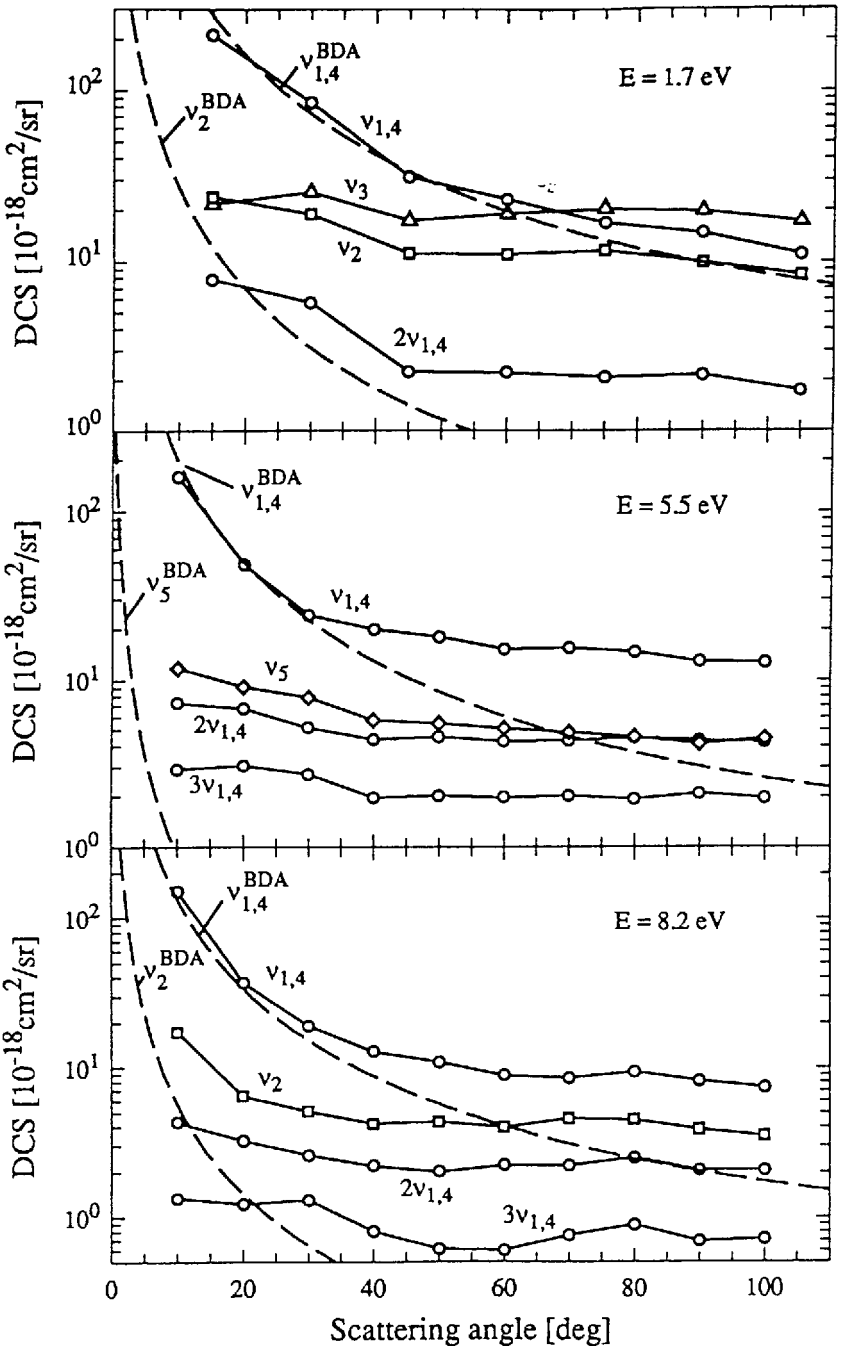


Figure 1. Comparison of measured values of DCSs for the vibrational excitation of CF_3Cl with those of the Born dipole calculation (BDA), at three points of collision energy E. The symbol ν_i means the ith normal mode and $\nu_{1,4}$ denotes the sum of the cross sections for ν_1 and ν_4. (Mann and Linder (1992), printed with permission.)

Downloaded At: 17:04 21 January 2011

Dipole matrix element squared for IR-active modes of vibration calculated from the IR intensity A and the vibrational frequency ω.

Molecule	Normal mode	ω† (cm^{-1})	A† (km mol^{-1})	(dipole matrix element)^2 (10^{-3} au)
H_2O	ν_1	3657	2·93	0·0495
	ν_2	1595	62·5	2·42
	ν_3	3756	41·7	0·686
H_2S	ν_1	2615‡		$1{\cdot}34\times10^{-3}$§
	ν_2	1183		$1{\cdot}50\times10^{-2}$‖
	ν_3	2626		$7{\cdot}08\times10^{-6}$§
CO_2	ν_2	667	47·8	4·43
	ν_3	2349	498·7	13·1
N_2O	ν_1	1285	59·1	2·84
	ν_2	589	8·20	0·860
	ν_3	2224	289	8·03
NH_3	ν_1	3337	4·9	0·091
	ν_2	950	148	9·62
	ν_3	3444	3·2	0·057
	ν_4	1627	27·1	1·03
CH_4	ν_3	3019	65·5	1·34
	ν_4	1311	31·8	1·50
CF_4	ν_3	1283	935·3	45·0
	ν_4	632	12·3	1·20
SiH_4	ν_3	2191	320·5	9·03
	ν_4	914	296·3	20·0
SF_6	ν_3	948	1361	88·7
	ν_4	615	74	7·4
CF_3Cl	ν_1	1102	561	31·4
	ν_2	783	35	2·8
	ν_4	1210	672	34·3
	ν_5	560	3·1	0·34

† Bishop and Cheung (1982), except for H_2S.
‡ Shimanouchi (1972).
§ Calculated with the dipole derivative determined by Lechuga-Fossat *et al.* (1984).
‖ Calculated with the dipole derivative determined by Emerson and Eggers (1962).

From the table of A and ω compiled by Bishop and Cheung (1982), the dipole matrix element squared is calculated as in the table. The table shows that, in the case of CF_3Cl, the dipole matrix elements for ν_1 and ν_4 are much larger than those for ν_2 and ν_5. This may be the main reason for the good applicability of the Born dipole theory to the excitation of the $\nu_{1,4}$ modes of vibration in the $e+CF_3Cl$ collision. In the table, we show the dipole matrix element for a number of polyatomic molecules of some interest. The extent of the dominance of the dipole interaction in the vibrational excitation can be estimated from the table.

5. Examples of calculation

For the electron-impact vibrational excitation of polyatomic molecules, a very limited number of theoretical studies have been reported so far, except for the Born-type calculations. Jain and Thompson (1983, 1984), and recently Gianturco and his colleagues, applied the vibrationally sudden approximation to the calculation for

Downloaded At: 17:04 21 January 2011

H_2O, H_2S and CH_4. The present author and his group calculated the vibrational cross-section of H_2O and H_2S, based on the rotationally sudden and vibrationally close-coupling method. Some special attention has been given to the vibrational excitation of CO_2 (particularly the threshold structure and the resonance in the cross-section). Several workers have tried to calculate the vibrational cross-section of CO_2 (Morrison and Lane 1979, Thirumalai *et al.* 1980, 1981, Thirumalai and Truhlar 1981, Whitten and Lane 1982), but the results are very fragmentary (i.e. only for a limited region of energy and scattering angle). There are some other papers discussing resonance effects in the vibrational excitation, which is not discussed in the present paper. In the following, the theoretical results for H_2O, H_2S and CH_4 are presented, together with the corresponding experimental data.

5.1. H_2O

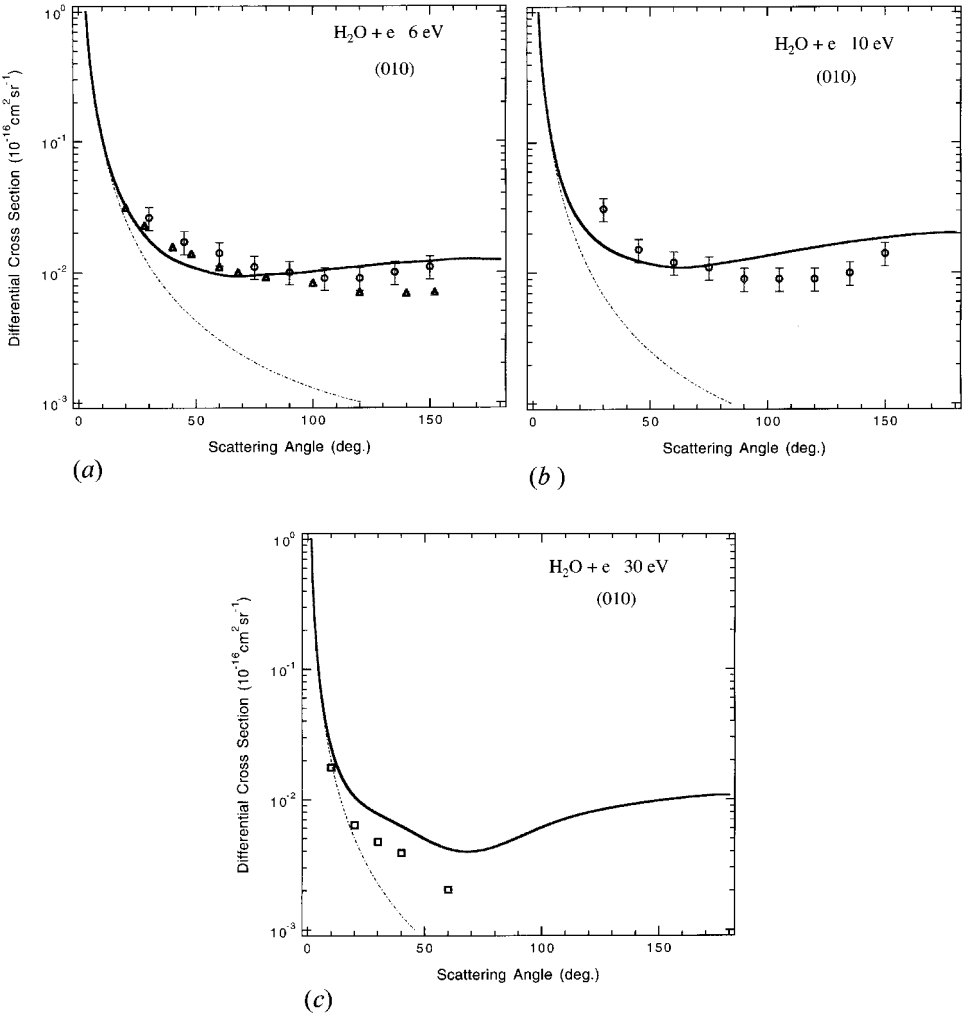
Recently Nishimura and Itikawa (1995) calculated the vibrational excitation cross-section of H_2O using the rotationally sudden and vibrationally close-coupling method. They solved the scattering equations (2.21) by taking the initial and the final vibrational states to be coupled (i.e. a two-state close-coupling approximation). They took an interaction potential composed of three parts: the electrostatic, exchange and polarization parts. The electrostatic potential was calculated accurately with the use of an *ab-initio* multicentred wavefunction of the molecule. Use was made of a local model potential for the electron exchange and target polarization: the Hara-type free-electron-gas exchange potential (3.15) for the former and the correlation–polarization potential (3.18) for the latter. The interaction matrix element with respect to the vibrational states was evaluated from the first-order derivative of the potential as in equation (3.9).

Downloaded At: 17:04 21 January 2011

The resulting DCS at 6, 10 and 30 eV are shown in figures 2 and 3. The cross-section was calculated for the excitation of the lowest excited state of the three different modes: symmetric stretching (100), bending (010), and antisymmetric stretching (001) modes. The excitation energies of the (100) and (001) modes are too close to each other to be separated experimentally. The experimental cross-section for the stretching modes is the cross-section combined for the (100) and (001) excitations (designated as (100)+(001) hereafter). As for the theoretical cross-section, we show in the figure the sum of the (100) and (001) cross-sections together with the individual cross-sections.

In the figures, two sets of experimental data are compared with the calculation. Shyn *et al.* (1988) measured the vibrational cross-section at 2·2–20 eV. Furlan *et al.* (1991) reported their measurement of DCS at 30 and 50 eV. Their DCSs, however, are available only at 10–60°. There is a generally good agreement between the theory and the experiment, except for the DCS for the stretching modes at 6 eV. The disagreement may be ascribed to a resonance effect and is discussed below in relation to the integral cross-section. For stretching vibrations, there is no significant difference in the magnitudes of the cross-sections for the symmetric (100) and the antisymmetric (001) modes. A systematic difference, however, is seen in the angular dependence of the cross-sections for the two modes. This may be a reflection of the difference in the symmetry of those modes.

As mentioned above, Jain and Thompson (1983) applied a vibrationally sudden approximation to the calculation of the vibrational cross-section of H_2O. They used the same procedure for constructing the interaction potential as Nishimura and Itikawa did. The molecular wavefunctions used by the two groups, however, are different from each other. Jain and Thompson calculated the cross-section at 1–10 eV

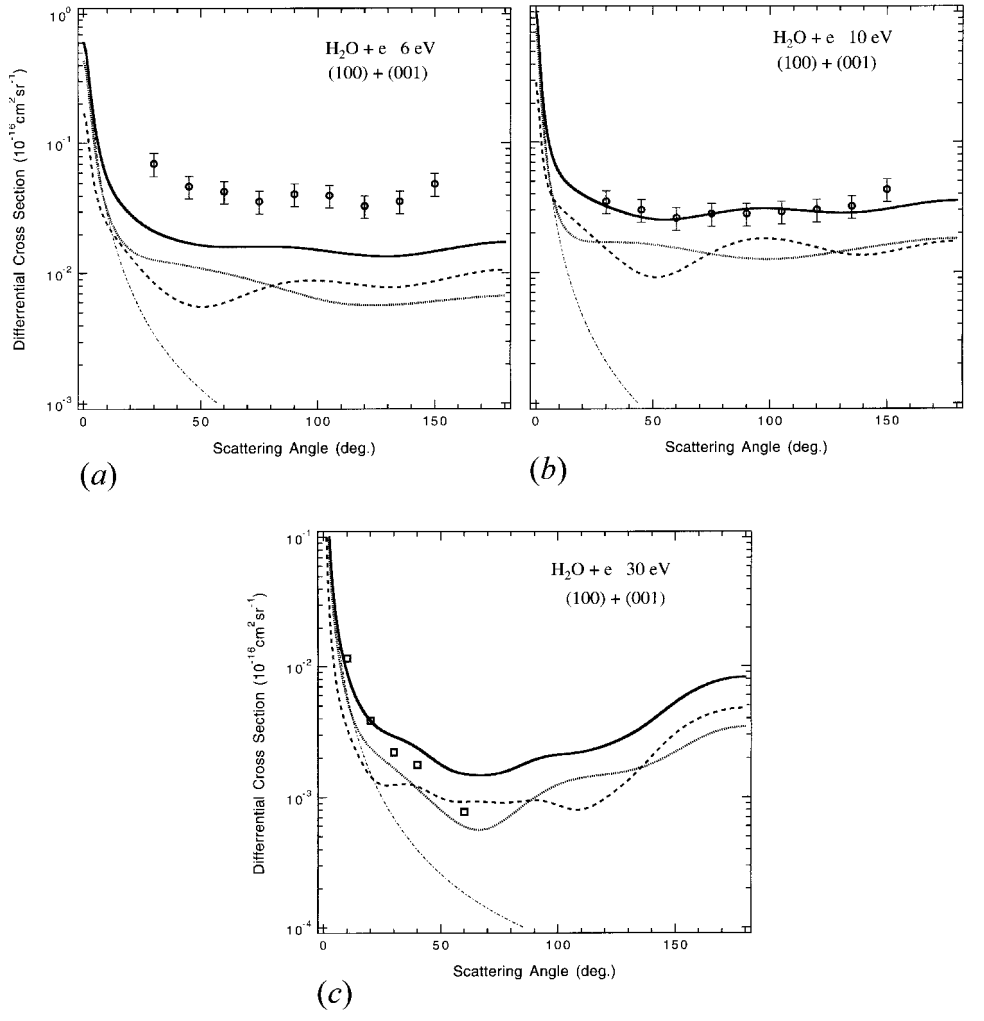


Downloaded At: 17:04 21 January 2011

Figure 2. DCSs for the vibrational excitation of bending mode of H_2O at (*a*) 6 eV, (*b*) 10 eV and (*c*) 30 eV. Theoretical calculations by Nishimura and Itikawa (1995) (——) and Jain and Thompson (1983) (△) are compared with experimental data obtained by Shyn *et al.* (1988) (○) and Furlan *et al.* (1991) (□). Also shown are the results of the Born dipole calculation (–·–).

but reported the DCS at the energies less than 8 eV. Furthermore, they obtained cross-sections for only the (100) and (010) modes. A comparison of the (010) DCS at 6 eV shows good agreement between the two sets of calculation (see figure 2(*a*)). Another comparison at 8 eV for (100) DCS (not shown here, but see the paper by Nishimura and Itikawa (1995)) shows, however, a somewhat large discrepancy in the large-angle region. The latter disagreement may arise from the difference in the target wavefunctions used.

In the figures, a comparison is also made with the Born approximation with a dipole interaction. Since the dipole interaction dominates in the forward scattering, the Born method gives almost the same values of DCS as the close-coupling calculation in the region with $\theta < 20^\circ$ for the (010) and $\theta < 5^\circ$ for the (100)+(001) modes. As the scattering angle increases, the Born DCS falls rapidly. The dipole

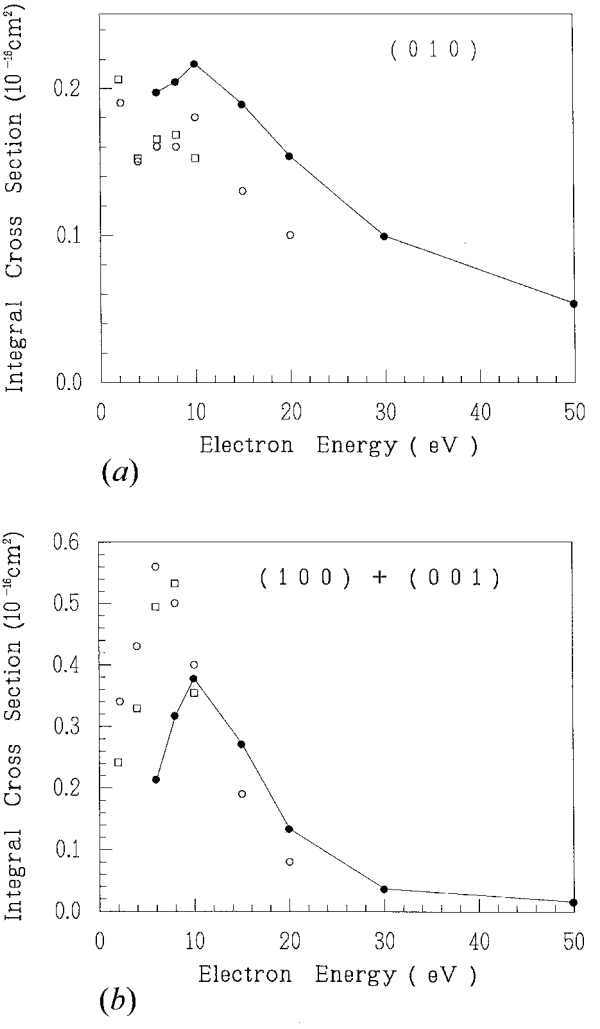


Downloaded At: 17:04 21 January 2011

Figure 3. DCSs for the vibrational excitation of stretching modes of H_2O at (*a*) 6 eV, (*b*) 10 eV and (*c*) 30 eV. The experimental values (obtained by Shyn *et al.* (1988) (○) and Furlan *et al.* (1991) (□) correspond to the sum of the cross-sections for the symmetric (100) and antisymmetric (001) modes. Theoretical results of Nishimura and Itikawa (1995) are given for the sum (100)+(001) (——) and for each (100) (– – –) and (001) (-----) modes. Also shown are the results of the Born dipole calculation for the sum of the process, (100)+(001) (–·–).

matrix element for the stretching modes is small compared with that for the bending mode (see the table). This makes the usefulness of the Born dipole approximation limited to the narrower angle region for the stretching modes.

In figure 4, the ICS obtained by Nishimura and Itikawa (1995) is compared with two sets of experimental data (Seng and Linder 1976, Shyn *et al.* 1988). For the bending mode, the theoretical ICS is larger than the experimental cross-sections by 20–50%. We have much better agreement between the DCS obtained by the close-coupling calculation and the experiment of Shyn *et al.*, as far as the latter cross-sections are available (see figures 2(*a*) and (*b*)). A large part of the difference in ICSs therefore comes from the contributions of DCS at the forward and backward



Downloaded At: 17:04 21 January 2011

Figure 4. ICSs for the vibrational excitation of H_2O for the (*a*) bending and (*b*) stretching modes. Theoretical calculations by Nishimura and Itikawa (1995) (—·—) are compared with the experimental results of Seng and Linder (1976) (□) and Shyn *et al.* (1988) (○).

scattering angles for which no DCS could be measured. In particular, in this case, the theory shows that the dipole interaction results in a large DCS in the forward direction. This makes an extrapolation of the experimental DCS towards $\theta = 0^\circ$ very difficult. For the stretching modes, both the calculation and the experiment show a peak as a function of collision energy. The peak position of the theoretical ICS, however, is located at a higher energy by a few electronvolts than that of the experimental peak. This peak is usually interpreted as a shape resonance, which is caused by a temporary capture of the colliding electron in the potential of the target molecule (Seng and Linder 1976). To reproduce such a resonance, a more elaborate treatment would be necessary both for the interaction and for the collision dynamics.

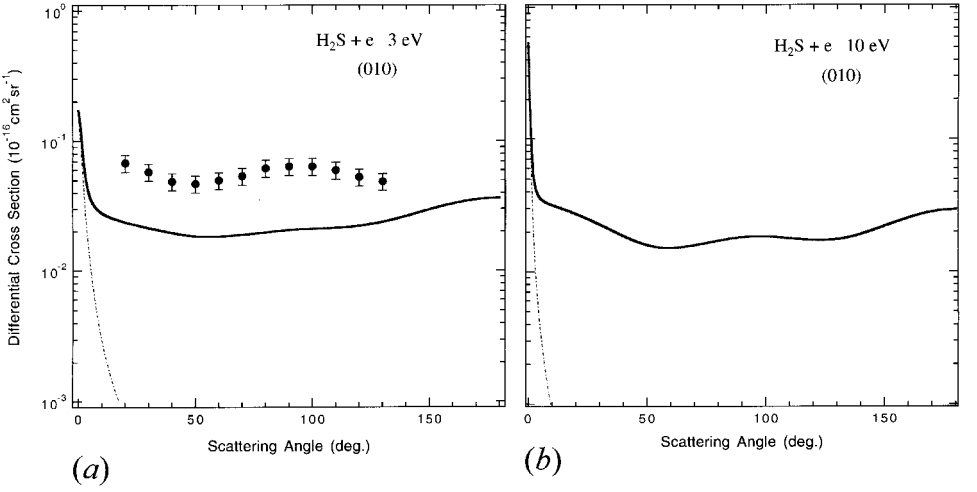


Figure 5. DCSs for the vibrational excitation of the bending mode of H_2S at (*a*) 3 eV and (*b*) 10 eV. Theoretical calculations by Nishimura and Itikawa (1996) (——) are compared with experimental data obtained by Gulley *et al.* (1993) (●). Also shown are the results of the Born dipole calculation (–·–).

Downloaded At: 17:04 21 January 2011

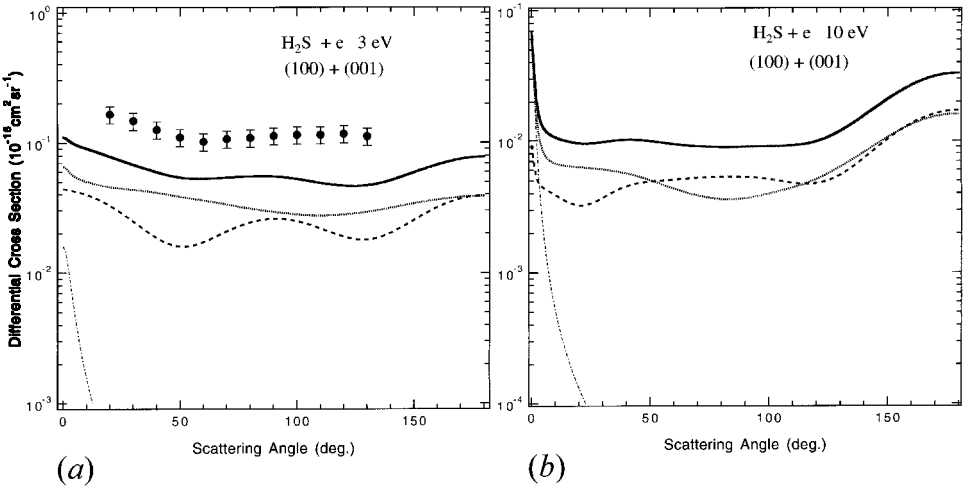


Figure 6. DCSs for the vibrational excitation of stretching modes of H_2S at (*a*) 3 eV and (*b*) 10 eV. The experimental values (Gulley *et al.* 1993) (●) correspond to the sum of the cross sections for the symmetric (100) and antisymmetric (001) modes. Theoretical results of Nishimura and Itikawa (1996) are given for the sum (100)+(001) (——) and for each (100) (– – –) and (001) (-----) modes. Also shown are the results of the Born dipole calculation for the sum of the process, (100)+(001) (–·–).

5.2. H_2S

Nishimura and Itikawa (1996) have extended their calculation of H_2O to H_2S. The two molecules have similar structure, but different number of electrons. Figures 5 and 6 show the DCSs at 3 and 10 eV. Gulley *et al.* (1993) reported their experimental result of the vibrational excitation of H_2S. They measured, however, the DCSs at only 2 and 3 eV and obtained no ICS. The comparison of theory and experiment at 3 eV (figures 5(*a*) and 6(*a*)) is rather disappointing, when the fairly good agreement obtained in the

case of H_2O is considered. The discrepancy may be attributed to a resonance effect. In fact, Rohr (1978) experimentally found a broad peak at 2·3 eV, which he suggested to be a shape resonance. Another possible reason for the discrepancy is the inaccuracy of the target wavefunction employed in the calculation. The wavefunction was optimized at the self-consistent field (SCF) level. The intramolecule correlation would be more important in H_2S than in H_2O.

Jain and Thompson (1984) extended their vibrationally sudden calculation to H_2S. Again they calculated cross-sections only for the excitation of (100) and (010) modes. Their DCS is available only at 2 eV for (010) and at 2 and 3 eV for (100) excitations. When a comparison is made between the (100) DCSs at 3 eV of Nishimura and Itikawa and of Jain and Thompson (not shown here, but see the paper by Nishimura and Itikawa (1996)), the latter cross-section is larger than the former. The Jain–Thompson DCS is too large compared even with the experimental DCS for (100)+(001).

In figures 5 and 6, we also show the Born dipole cross-section for comparison. For H_2S, the dipole matrix element is very small (see the table). The Born dipole approximation produces a meaningful value only in the very vicinity of $\theta = 0^\circ$.

Nishimura and Itikawa (1996) calculated the ICS for the excitations of (100), (010) and (001) modes of vibration at 3–30 eV. No corresponding experimental data are available. Jain and Thompson (1984) reported the theoretical ICS at 0·5–7 eV, but for only (100) and (010) modes. The results of the two sets of calculations (the Nishimura–Itikawa and Jain–Thompson data) disagree with each other as in the case of DCS mentioned above. This difference probably comes from the difference in the target wavefunctions used. For a more detailed study, further experimental data would be helpful.

Downloaded At: 17:04 21 January 2011

5.3. CH_4

The only theoretical work (except for a Born-type calculation) on the vibrational excitation of CH_4 is the recent calculation by Althorpe *et al.* (1995). They employed the vibrationally sudden approximation, supplemented by a non-adiabaticity correction near threshold. They took into account the effect of electron exchange rigorously but used a local model potential for the target polarization.

Figure 7 shows the theoretical results of the ICS for the (ν_1, ν_3) modes and (ν_2, ν_4) modes. Experimentally it is very difficult to separate the $\nu_1(\nu_2)$ from the $\nu_3(\nu_4)$ modes. In the figure, the sum of the cross-sections for the ν_1 and ν_3 (and also ν_2 and ν_4) is compared with the corresponding experimental values (Tanaka *et al.* 1983, Shyn 1991). The theory reproduces the broad peak at around 7·5 eV in the experimental data. There are some disagreements, however, in the absolute magnitudes of the theoretical and the experimental cross-sections. It should be noted that the experimental values do not agree with each other and have a large uncertainty (30–50% for the Tanaka *et al.* data and 25–29% for the Shyn data). A more detailed comparison could be made for DCS, but Althorpe *et al.* reported no DCS in their paper.

For the IR-active modes of vibration (i.e. ν_3 and ν_4), the theoretical cross-sections of Althorpe *et al.* show a sharp peak just above the respective threshold. This kind of threshold structure has been studied experimentally (Rohr 1980, Sohn *et al.* 1983, Lunt *et al.* 1994), but the experimental data available near threshold are only DCSs at a few scattering angles. In the figure we also show the vibrational cross-section for the ν_3 and ν_4 modes calculated in the Born approximation with a dipole interaction. The energy dependence of the cross-section obtained by Althorpe *et al.* near threshold is close to that of the Born dipole one. This may suggest that the dipole interaction plays

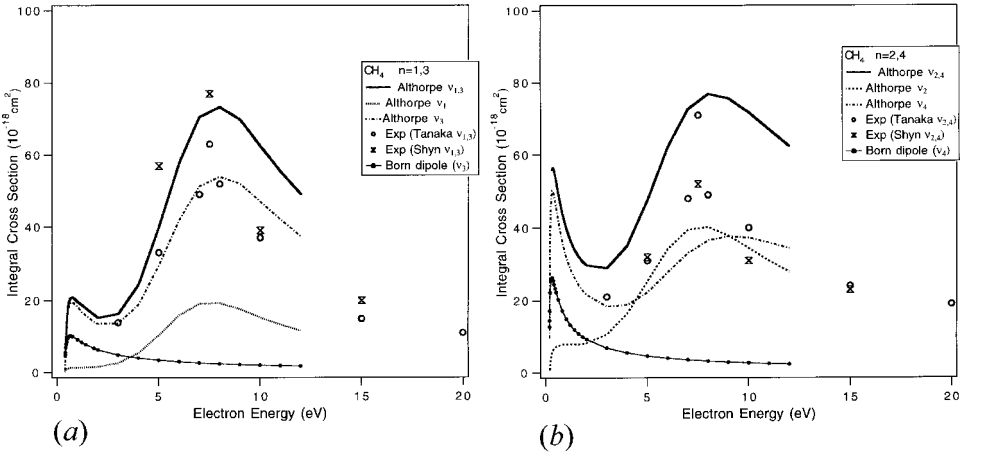


Figure 7. ICCs for the vibrational excitation of CH_4 for the (*a*) ν_1, ν_3 and (*b*) ν_2, ν_4 modes. Here ν_i means the *i*th normal mode and $\nu_{i,j}$ indicates the sum of the cross-sections for ν_i and ν_j. Theoretical calculations by Althorpe *et al.* (1995) are compared with experiment by Tanaka *et al.* (1983) and Shyn (1991). The results of the Born dipole calculation are also shown for the IR-active modes, ν_3 and ν_4.

Downloaded At: 17:04 21 January 2011

a significant role in the vibrational excitation of the ν_3 and ν_4 modes at the energies near threshold. This would be studied in more detail, if we could make a comparison of DCSs.

6. Concluding remarks

In the present paper, an approach to cross-section calculation is presented for the electron-impact vibrational excitation of polyatomic molecules. It is based on the FNO (in other words, the rotationally sudden) approximation. The resulting scattering equations are solved by a close-coupling method or by a vibrationally sudden approximation. Cross-sections obtained in the calculations along this approach for H_2O, H_2S and CH_4 are shown graphically and compared with experimental data. Agreement between the theoretical and experimental values is generally good. In some cases, however, one sees significant disagreement. The largest uncertainty on the theoretical side is ascribed to the determination of the interaction matrix elements. For the vibrational excitation, we need to know the dependence of the electron–molecule interaction on the nuclear configuration of the molecule. We have to have an accurate molecular wavefunction not only at the equilibrium position of the nuclei but also for their non-equilibrium positions. It is often said that an SCF-type wavefunction is not sufficiently reliable to produce an IR intensity (i.e. a derivative of dipole moment), although it can give a fairly good value of dipole moment (Amos 1987; Stanton *et al.* 1991). We have to take into account carefully the intramolecule electron correlation to obtain the nuclear-coordinate dependence of the interaction potential. The molecular vibration is not necessarily harmonic. To obtain an accurate interaction matrix, the anharmonicity should be considered also. Moreover, we have to develop a more elaborate, but still tractable, method of treatment of target polarization. (For the effect of electron exchange, a rigorous treatment can be made, if necessary.)

For collision dynamics, some kinds of elaborate treatment have been proposed for diatomic molecules (see the book edited by Huo and Gianturco (1995)). When the collision energy is low, the motions of the colliding electron and the molecular nuclei cannot totally be separated (i.e. the non-adiabatic effect). When the collision energy is

high, an excitation of electronic state of the molecule may have an effect on the vibrational excitation. Some attempts to include these effects in the cross-section calculation have been tried for diatomic molecules. In principle, those methods can be extended to polyatomic molecules, although leading to a very time-consuming calculation. Before that, it is worth applying a simpler approach, such as shown in the present paper, to a wide range of vibrational excitation of molecules to see the general trend of the process and to find where the refinement is needed.

Acknowledgement

The author would like to thank Tamio Nishimura for the collaboration in the work reported in the present review article and for the preparation of the figures therein.

References

Althorpe, S. C., Gianturco, F. A., and Sanna, N., 1995, *J. Phys.* B, **28**, 4165.
Altmann, S. L., and Cracknell, A. P., 1965, *Rev. mod. Phys.*, **37**, 19.
Amos, R. D., 1987, *Ab Initio Methods in Quantum Chemistry*, edited by K. P. Lawley (New York: Wiley), p. 99.
Bishop, D. M., and Cheung, L. M., 1982, *J. Phys. Chem. Ref. Data*, **11**, 119.
Burke, P. G., Chandra, N., and Gianturco, F. A., 1972, *J. Phys.* B, **5**, 2212.
Christophorou, L. G., Datskos, P. G., and Carter, J. G., 1991, *Chem. Phys. Lett.*, **186**, 11.
Davis, H. T., and Schmidt, L. D., 1972, *Chem. Phys. Lett.*, **16**, 260.
Emerson, M. T., and Eggers, D. F., Jr., 1962, *J. chem. Phys.*, **37**, 251.
Furlan, M., Hubin-Franskin, M.-J., Delwiche, J., and Collin, J. E., 1991, *J. chem. Phys.*, **95**, 1671.
Gianturco, F. A., 1995, *The Physics of Electronic and Atomic Collisions*, edited by L. J. Dube, J. B. A. Mitchell, J. W. McConkey and C. E. Brion (Woodbury, New York: American Institute of Physics), p. 211.
Gianturco, F. A., and Jain, A., 1986, *Phys. Rep.*, **143**, 347.
Gianturco, F. A., Thompson, D. G., and Jain, A., 1995, *Computational Methods for Electron-Molecule Collisions*, edited by W. M. Huo and F. A. Giantuco (New York: Plenum), p. 75.
Gulley, R. J., Brunger, M. J., and Buckman, S. J., 1993, *J. Phys.* B, **26**, 2913.
Hara, S., 1967, *J. phys. Soc. Japan*, **22**, 710.
Huo, W. M., and Gianturco, F. A. (editors), 1995, *Computational Methods for Electron–Molecule Collisions* (New York: Plenum).
Itikawa, Y., 1971, *Phys. Rev.* A, **3**, 831; 1974, *J. phys. Soc. Japan*, **36**, 1121.
Jain, A., and Thompson, D. G., 1983, *J. Phys.* B, **16**, L347; 1984, *Ibid.*, **17**, 443.
Kimura, M., Inokuti, M., and Dillon, M. A., 1993, *Adv. chem. Phys.*, **84**, 193.
Krajcar-Bronic, I., and Kimura, M., 1995, *J. chem. Phys.*, **103**, 7104.
Lechuga-Fossat, L., Flaud, J.-M., Camy-Peyret, C., and Johns, J. W. C., 1984, *Can. J. Phys.*, **62**, 1889.
Lucchese, R. R., and Gianturco, F. A., 1996, *Int. Rev. phys. Chem.*, **15**, 429.
Lunt, S. L., Randell, J., Ziesel, J. P., Mrotzek, G., and Field, D., 1994, *J. Phys.* B, **27**, 1407.
Mann, A., and Linder, F., 1992, *J. Phys.* B, **25**, 1621.
Mason, N. J., Johnstone, W. M., and Akther, P., 1994, *Electron Collisions with Molecules, Clusters, and Surfaces*, edited by H. Ehrhardt and L. A. Morgan (New York: Plenum), p. 47.
Morrison, M. A., and Lane, N. F., 1979, *Chem. Phys. Lett.*, **66**, 527.
Morrison, M. A., and Sun, W., 1995, *Computational Methods for Electron–Molecule Collisions*, edited by W. M. Huo and F. A. Giantuco (New York: Plenum), p. 131.
Nishimura, T., and Itikawa, Y., 1995, *J. Phys.* B, **28**, 1995; 1996, *Ibid.*, **29**, 4213.
Padial, N. T., and Norcross, D. W., 1984, *Phys. Rev.* A, **29**, 1742.
Rohr, K., 1978, *J. Phys.* B, **11**, 4109; 1980, *Ibid.*, **13**, 4897.
Seng, G., and Linder, F., 1976, *J. Phys.* B, **9**, 2539.

Downloaded At: 17:04 21 January 2011

SHIMANOUCHI, T., 1972, *Tables of Molecular Vibrational Frequencies Consolidated*, Vol. I, National Standard Reference Data Series, National Bureau of Standards, Vol. 39 (Washington, DC; US Government Printing Office).
SHYN, T. W., 1991, *J. Phys.* B, **24**, 5169.
SHYN, T. W., CHO, S. Y., and CRAVENS, T. E., 1988, *Phys. Rev.* A, **38**, 678.
SOHN, W., JUNG, K., and EHRHARDT, H., 1983, *J. Phys.* B, **16**, 891.
STANTON, J. F., WATTS, J. D., and BARTLETT, R. J., 1991, *J. chem. Phys.*, **94**, 404.
TANAKA, H., KUBO, M., ONODERA, N., and SUZUKI, A., 1983, *J. Phys.* B, **16**, 2861.
THIRUMALAI, D., ONDA, K., and TRUHLAR, D. G., 1980, *J. Phys.* B, **13**, L619; 1981, *J. chem. Phys.*, **74**, 6792.
THIRUMALAI, D., and TRUHLAR, D. G., 1981, *J. chem. Phys.*, **75**, 5207.
WHITTEN, B. L., and LANE, N. F., 1982, *Phys. Rev.* A, **26**, 3170.

Downloaded At: 17:04 21 January 2011