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Franck–Condon Matrix Elements for Bound-Continuum Vibrational Transitions Calculated by Numerical Integration and Basis Set Expansion Techniques

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Franck–Condon factor distributions for bound-to-continuum transitions of one-dimensional vibrational states are calculated by a) using numerical integration, b) employing a finite number of square integrable harmonic oscillator functions. The methods are generally applicable to any kind of bound or repulsive potential involved. Results are presented and compared to model potential calculations previously reported by Krüger [1].

Key words: Franck–Condon factors – Bound-continuum vibrational transitions

1. Introduction

The aim of this paper is to show that it is possible to compute accurate Franck–Condon factor distributions employing well known methods generally used to solve one-dimensional vibrational problems involving bound or scattering states. This work is an extension of procedures employed in this laboratory [2, 3] and presents an alternative to a previous work of Krüger [1], who calculated bound-to-continuum Franck–Condon matrix elements employing uniform semiclassical techniques. We used two completely different methods and compared our results to those of Krüger [1]. The first makes use of numerical integration techniques, while the second constructs the correct Franck–Condon factor distribution from a given set of individual Franck–Condon factors which can be easily computed by standard bound state vibration programs involving any kind of basis functions, if they are capable of representing the correct potential energy for arbitrary internuclear distances.

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2. Method 1

The bound as well as the repulsive system are treated numerically. This is done by solving numerically the one-dimensional differential equation

$$\frac{d^2\psi(R)}{dR^2} = 2\mu(V(R) - E)\cdot\psi(R) \tag{1}$$

using a difference formula according to Numerov [4]. The bound system, which involves the boundary conditions

$$\psi^b(R = R_1) = 0 \quad \text{and} \quad \psi^b(R_n = R_1 + n\cdot h) = 0 \tag{2}$$

(with $h = (R_n - R_1)/n$, n = number of grid points) is treated here by a method developed by Cooley [5]. For this purpose the range from $R_1 = 4.8\ a_0$ to $R_n = 10.0\ a_0$ is divided into 2000 equidistant parts with $h = 2.6\cdot 10^{-3}\ a_0$. As bound potential we used a Morse potential

$$V(R) = D\cdot(1 - e^{-\alpha(y-1)})^2 \tag{3}$$

with $y = R/R_m$ and in order to compare our results with those given by Krüger we chose the same set of potential parameters ($\alpha = 14$, $R_m = 3$ Å $= 5.6692569\ a_0$, $D = 0.061567$ a.u.). Our numerically calculated vibrational energy for the $v = 0$ state is 273.61456 cm^{-1}, which differs by $5\cdot 10^{-5}\ \text{cm}^{-1}$ from the exact result. The continuum functions for the repulsive potential curve

$$V(R) = V_0\cdot e^{-\alpha y} \tag{4}$$

(with $V_0 = 1\cdot 10^5$ eV while α and R_m are the same as for the Morse potential) satisfy the boundary conditions

$$\psi^c(R = R_1) = 0 \quad \text{and} \quad \psi^c(R_2 = R_1 + h) = A\cdot e^{(V(R_2)-E)\cdot(R_2-R_T)} \tag{5}$$

with R_T being the turning point. The resulting differential equation can be solved using the analogous difference formula as for the bound system which is a well known procedure in scattering theory [6, 7]. Since we used the same grid points for this system as for the bound system the Franck–Condon factors (FCF)

$$\text{FCF} = \left| \int_{R_1}^{R_n} \psi^c(R)\cdot\psi^b(R)\, dR \right|^2 \tag{6}$$

can be calculated directly via Simpson's numerical integration technique.

3. Method 2

It has already been demonstrated by Hazi and Taylor [8] that a vibration-Hamiltonian having a continuous spectrum can be treated by a finite number of square integrable functions. Here we show that it is equally possible to handle bound-continuum transitions by bound state methods [3]. One of the standard methods for constructing the vibration-Hamiltonian is used. In the first step the method of Harris *et al.* [9] is employed and R (the operator for the position coordinate) defined as $R = R' - R_0$ (R_0 = reference-point) is diagonalized in the basis of harmonic oscillator functions yielding eigenvalues R_i. In the limit of a complete set $V(R_i/D)$ (D being a scaling parameter here chosen to be optimized for the bound state) is diagonal and the matrix $V'(R/D)$ can be obtained by backtransformation

$$V'(R/D) = C\cdot V(R_i/D)\cdot C^{-1} \quad (C \text{ being the eigenvector matrix of } R) \tag{7}$$

(This gives a correct representation of the potential energy for small and large values of R in contrast to an expansion of V in powers of R, which is not advisable in this case because such power series lead to artificial oscillations for larger values of R.) The errors inherent to such a procedure have been described elsewhere [9]. The Hamiltonian is then given by

$$H = \frac{D^2}{2\mu}\frac{d^2}{dR^2} + V(R/D) \tag{8}$$

The diagonalization of the bound state Hamiltonian yields a set of approximate variational bound state energies and eigenvectors (the calculated frequency for the lowest level is 273.615 cm^{-1} which agrees with the exact result to the decimals

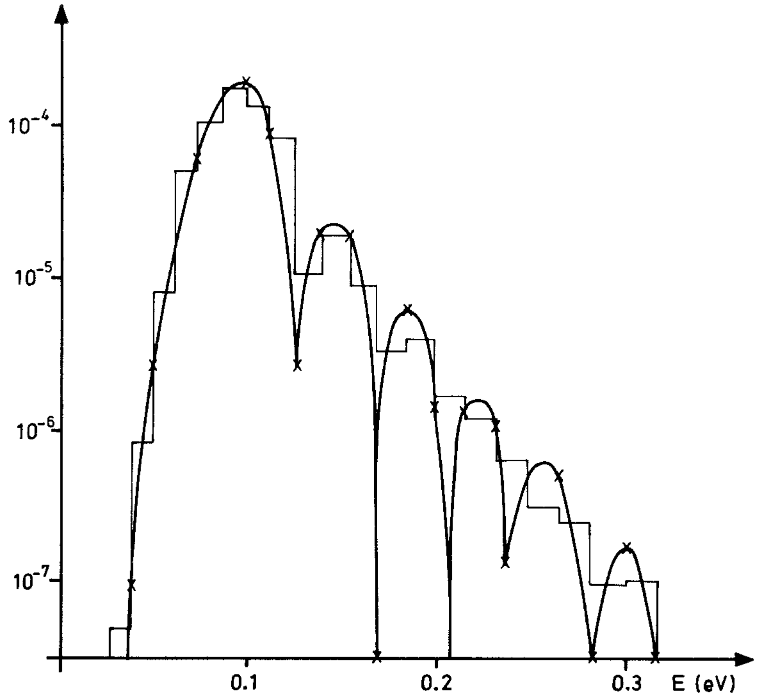

Fig. 1. Stieltjes histogram and Franck–Condon factor distribution according to formula (11) for calculations including 120 basis functions. In Figs. 1–3 the oscillator strength distribution is given in a dimensionless form by multiplying $f(E)^2$, with $\hbar^2/\mu R_m^2$ as it has been done in Krüger's paper [1]

shown) whereas the H-operator for the continuous states yields a set of discrete pseudostate energies and corresponding wavefunctions. These are known to be good approximations to the exact continuum wavefunctions over a large range of R/D values depending on the number of basisfunctions [8]. To get an energy dependent Franck–Condon factor distribution two techniques are employed. The first is analogous to one of the methods used in photoionisation cross-section calculations [10] and provides a histogram approximation to the correct distribution. But in contrast to the so-called Stieltjes imaging method described in [10] we assume here that the pseudostate energies and the Franck–Condon factors already yield an approximate discrete representation of the cumulative Franck–Condon factor distribution

$$F(\varepsilon) = \int_0^{\varepsilon} f(\varepsilon')\, d\varepsilon' \tag{9}$$

from which the Franck–Condon factor distribution is obtained by differentiation in the Stieltjes sense. In the theory of Stieltjes imaging [8] the histogram is computed

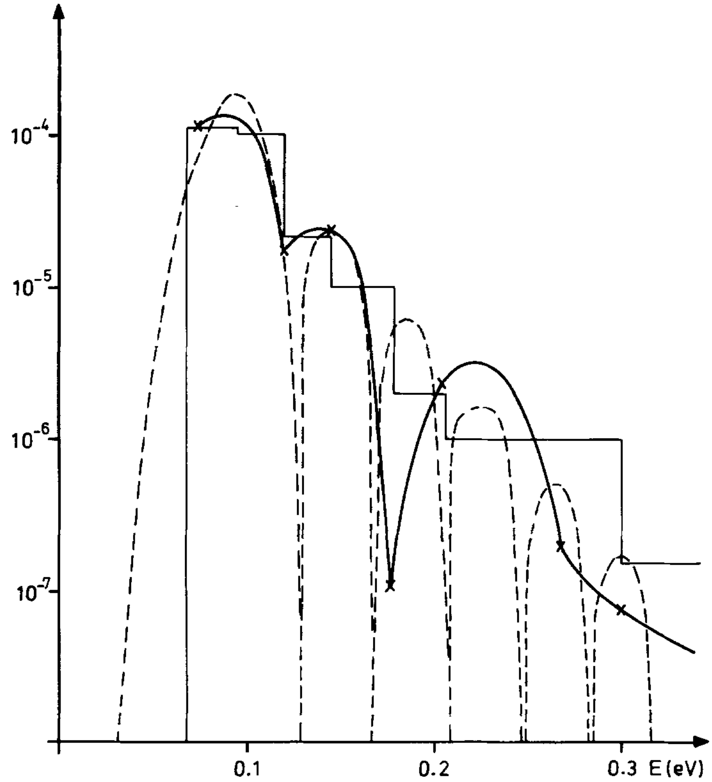

Fig. 2. Stieltjes histogram and Franck–Condon factor distribution according to formula (11) including 10 basis functions. The correct Franck–Condon factor distribution is given by the dotted line

from a small number of converged moments of the cumulative oscillator strength distribution given in an approximate discrete form by the computed pseudoenergies and oscillator strengths. Generally this technique has the effect of smoothing the input data, as can be seen from the used Stieltjes derivative formula

$$f(\varepsilon) = \frac{f_i(\varepsilon_i) + f_{i+1}(\varepsilon_{i+1})}{2(\varepsilon_{i+1} - \varepsilon_i)} \qquad \varepsilon_i < \varepsilon < \varepsilon_{i+1} \tag{10}$$

More structure can be retained by using the interpolation formula

$$f(\varepsilon_i) = \frac{2f(\varepsilon_i)}{\varepsilon_{i+1} - \varepsilon_{i-1}} \tag{11}$$

which should give a pointwise approximation to $f(\varepsilon)$ in the limit of great pseudostate energy density. A justification of this formula will be given in a subsequent

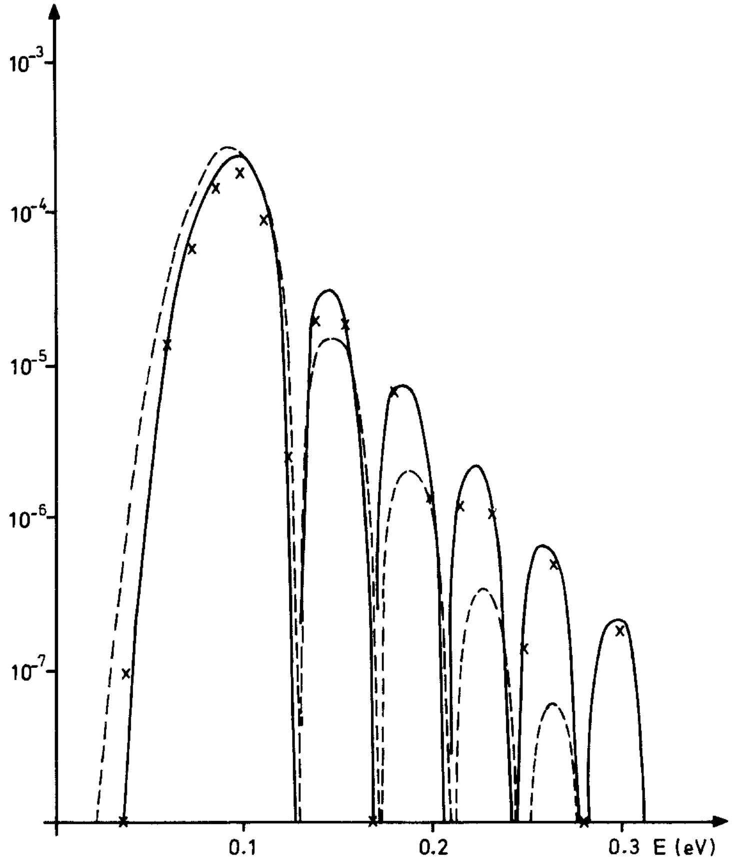

Fig. 3. Franck–Condon factor distribution calculated by numerical integration (full line) compared to the results of Krüger, adapted from Fig. 2 of Ref. [1]. The marked points indicate the Franck–Condon factor distribution calculated by Method 2

	(Ref. [1])	E(eV) Method 1	Method 2
Max. 1	0.090	0.095	0.098
Min. 2	0.130	0.128	0.124
Max. 2	0.147	0.145	0.146
Min. 3	0.172	0.168	0.168
Max. 3	0.187	0.185	0.183
Min. 4	0.211	0.206	0.206
Max. 4	0.227	0.223	0.223
Min. 5	0.249	0.243	0.247
Max. 5	0.265	0.260	0.258
Min. 6		0.280	0.282
Max. 6		0.298	0.299

Table 1. Location of the minima and maxima in the Franck–Condon factor distribution with respect to the energy. A comparison of the results calculated by Method 1 and Method 2 presented in this paper with those of Krüger as taken from Fig. 2 of Ref. [1]

publication.[1] Whereas the histogram approximation yields an envelope for the correct distribution (see Fig. 1) even if the number of basisfunctions is reduced to 10, the interpolation formula yields in the case that the density of the pseudostates is greater than the expected variations in the Franck–Condon factor distribution a correct pointwise image of the exact Franck–Condon factor distribution. If this condition is not met it is advisable to use the histogram approximation because otherwise the position and depth of the occurring minima is completely unreliable (see Fig. 2).

4. Discussion

The results of both methods are in good agreement with Krüger's "exact" values (Fig. 3). The overall structure of the Franck–Condon factor distribution is very similar with respect to the location of the maxima and minima (Table 1). But we find a difference concerning the fall-off of the maxima to the high energy side, which is not as strong in the methods presented as those in the approximation derived by Krüger [1]. The methods described here are flexible enough to be applicable to any kind of potential involved and thus provide a useful tool for the calculation of Franck–Condon factor distributions. Further it is easy to include the electronic transition moment, which might exhibit a strong variation with internuclear distance, as it has already been done for transitions between bound states [2, 11].

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[1] Formula (11) has been used previously by G. W. F. Drake, Astrophys. J. **184**, 145 (1973) in connection with the calculation of spontaneous bound-free transition of the $2p^2\ {}^3p^e$ state of H$^-$.

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