

COMMUNICATIONS

A quantitative study of non-Condon effects in the $S_2O \tilde{C} \rightarrow \tilde{X}$ emission spectrumF. Iachello^{a)} and F. Pérez-Bernal^{b)}*Center for Theoretical Physics, Yale University, New Haven, Connecticut 06520-8120*T. Müller and P. H. Vaccaro^{c)}*Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107*

(Received 17 December 1999; accepted 24 February 2000)

A novel technique has been developed for the quantitative study of vibronically-resolved transition intensities in polyatomic molecules beyond the Condon approximation. Matrix elements of coordinate-dependent transition moment operators are evaluated analytically with the pertinent vibrational wave functions obtained by means of Lie algebraic methods. Experimentally-observed $S_2O \tilde{C}^1A' - \tilde{X}^1A'(\pi^* - \pi)$ emission intensities, in conjunction with previous Franck–Condon calculations, reveal pronounced non-Condon effects for vibronic bands terminating on higher-lying vibrational levels of the ground electronic state. The transition dipole moment is examined as a function of both the S–O and S–S local stretching coordinates. © 2000 American Institute of Physics. [S0021-9606(00)01615-9]

The analysis of vibronic transition intensities, one of the primary tools used to unravel molecular structure, usually proceeds in a Franck–Condon framework, where electronic transitions are treated within a sudden approximation and the dependence of the electronic transition moment on nuclear coordinates is neglected (the Condon approximation).¹ Although this approach has been exploited extensively in traditional optical spectroscopy² as well as in many other areas,³ the calculation of multidimensional Franck–Condon factors has remained a difficult and computationally intensive task, with most reports published to date based upon an harmonic treatment of nuclear dynamics. Recently, we have introduced a method to analyze Franck–Condon transition intensities in polyatomic molecules quantitatively and have applied it to the interpretation of vibronically-resolved emission^{4,5} and absorption⁶ spectra for the triatomic disulfur monoxide (S_2O) species. Building upon Lie algebraic techniques, our method incorporates vibrational anharmonicity from the onset and provides a computationally efficient means for extracting dynamical and structural information from experimental data.⁵

Our previously reported Franck–Condon analyses of $S_2O \tilde{C}^1A' - \tilde{X}^1A'(\pi^* - \pi)$ emission spectra reproduced experimental intensities accurately for ground state features possessing up to ~ 10 quanta of excitation in the ν_2 S–S stretching mode. Theoretical predictions systematically overestimated the strength of vibronic bands terminating on

higher-lying vibrational levels of the \tilde{X}^1A' potential surface. Such discrepancies could not be accounted for by modification of parameters in the algebraic Hamiltonians used to describe the vibrational degrees of freedom or by more radical changes in underlying vibrational dynamics, including perturbative intensity borrowing mechanisms induced through isomerization or intramolecular vibrational relaxation, as no appreciable intensity attributable to interloping transitions is measured in this excitation region. This suggested that the Condon approximation may not be valid and that the dependence of the transition dipole operator on internal coordinates must be taken explicitly into account.

Non-Condon effects have been invoked in several areas of molecular dynamics and spectroscopy. They are thought to play a significant role in radiationless relaxation,⁷ Raman intensities,⁸ long-range electron transfer,⁹ and electronic transitions in the condensed phase.¹⁰ In studies of photodissociation dynamics, transition dipole functions have been derived from *ab initio* electronic structure calculations.¹¹ However, the present work constitutes the first quantitative study where the nuclear dependence of the transition dipole moment connecting two bound electronic states in a polyatomic molecules has been extracted directly from an extensive experimental data set.

The purpose of this communication is twofold: (i) to introduce a new approach for studying non-Condon effects in electronic transitions and (ii) to quantify non-Condon effects contributing to the intensities of $S_2O \tilde{C} \rightarrow \tilde{X}$ emission features that terminate on higher-lying \tilde{X}^1A' vibrational levels. Building upon the formalism and notation employed for our previous algebraic Franck–Condon analyses, the method consists of introducing a dipole moment function of the form $M(x) = M_0 e^{\beta x}$ for each ‘‘local’’ vibrational coordinate x ,

^{a)}Also at: Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107.

^{b)}Present address: Departamento de Física Aplicada e Ingeniería Eléctrica, Universidad de Huelva, Carretera Palos-La Rábida s/n, Palos de la Frontera, 21819 Huelva, Spain.

^{c)}Electronic mail: patrick.vaccaro@yale.edu

where x signifies the displacement from equilibrium configuration. While the Condon approximation¹ would require $M(x)$ to be a constant independent of x (i.e., $\beta=0$), non-Condon effects can be investigated by allowing $\beta \neq 0$. A Taylor-series expansion restricted to linear terms [$M(x) = M_0(1 + \beta x)$] would not be expected to be sufficient for the present investigation where a large range of vibrational quantum numbers ($\Delta v > 20$) and, thus, of nuclear coordinates is explored.

The evaluation of requisite transition matrix elements is accomplished in a manner very similar to that introduced previously,⁵ except that all overlap integrals between the two electronic configurations (for S_2O , \tilde{X}^1A' and \tilde{C}^1A')

$$T_{v'_1, v'_2, v'_3 \rightarrow v_1, v_2, v_3} = \langle \tilde{X}; v_1, v_2, v_3 | \tilde{C}; v'_1, v'_2, v'_3 \rangle \quad (1)$$

are replaced by the corresponding matrix elements of the transition dipole moment operator, \hat{M} :

$$M_{v'_1, v'_2, v'_3 \rightarrow v_1, v_2, v_3} = \langle \tilde{X}; v_1, v_2, v_3 | \hat{M} | \tilde{C}; v'_1, v'_2, v'_3 \rangle. \quad (2)$$

Here, the notation employed for vibrational quantum num-

bers is the same as that defined in our previous work⁵ where v_1 , v_2 , and v_3 refer to the collective S–O stretch, S–S stretch, and S–S–O bending modes, respectively. The integral in Eq. (2) converges for either sign of β provided that the associated wave functions decrease sufficiently rapidly as $x \rightarrow \infty$, a situation found to hold true for eigenfunctions of harmonic, Morse, and Pöschl–Teller potentials.

As described in our earlier investigations,⁵ the Lie algebraic approach affords a systematic means for expanding molecular eigenstates in terms of a “local oscillator” basis thereby allowing matrix elements such as those defined by Eqs. (1) and (2) to be formulated as simplified products of one-dimensional integrals. An analytical expression for the one-dimensional vibrational overlap integrals employed in Franck–Condon analyses [Eq. (1)] already has been reported.¹² The present incorporation of non-Condon effects [Eq. (2)] builds upon an explicit analytical formula for the quantity $\langle v | \hat{M} | v' \rangle$ as derived for two harmonic oscillators characterized by different frequencies, $\omega(\omega')$, and concavities, $\alpha(\alpha')$, as well as relative spatial displacement, Δ :

$$\begin{aligned} \langle v | \tilde{M} | v' \rangle &= \int_{-\infty}^{+\infty} \psi_v^*(\alpha; x) e^{\beta x} \psi_{v'}(\alpha'; x - \Delta) dx \\ &= \exp\left[-\frac{\Delta^2}{2} \left(\frac{\alpha'^2 \alpha^2}{\alpha'^2 + \alpha^2}\right)\right] \exp\left[\beta \Delta \frac{\alpha'^2}{\alpha'^2 + \alpha^2}\right] \exp\left[\frac{\beta^2}{4} \frac{2}{\alpha'^2 + \alpha^2}\right] \sqrt{\frac{2\alpha\alpha'n!n'}{\alpha'^2 + \alpha^2}} \sum_{k=0}^n \sum_{k'=0}^{n'} \sum_{\substack{j=n-k \\ \text{mod } 2}}^{0,1} \sum_{\substack{j'=n'-k' \\ \text{mod } 2}}^{0,1} (-1)^{k'} \\ &\quad \times (2\Delta)^{k+k'} \left(\frac{\alpha^2}{\alpha'^2 + \alpha^2}\right)^{k'} \left(\frac{\alpha'^2}{\alpha'^2 + \alpha^2}\right)^k \frac{\alpha'^{k'}}{\left(\frac{n'-k'-j'}{2}\right)! k'!} \left(\frac{2\alpha'^2}{\alpha'^2 + \alpha^2} - 1\right)^{(n'-k'-j')/2} \left(\frac{2\alpha'^2}{\alpha'^2 + \alpha^2}\right)^{j/2} \\ &\quad \times \frac{\alpha^k}{\left(\frac{n-k-j}{2}\right)! j! k!} \left(\frac{2\alpha^2}{\alpha'^2 + \alpha^2} - 1\right)^{(n-k-j)/2} \left(\frac{2\alpha^2}{\alpha'^2 + \alpha^2}\right)^{j/2} 2^{j-(n+n')/2} \left(\frac{\beta}{2} \sqrt{\frac{2}{\alpha'^2 + \alpha^2}}\right)^{j-j'} L_{j'}^{(j-j')} \left(-\frac{\beta^2}{\alpha'^2 + \alpha^2}\right), \end{aligned} \quad (3)$$

with $\alpha = \sqrt{(\mu\omega/\hbar)}$ defining the inverse oscillator length (concavity) for an harmonic oscillator of reduced mass μ and frequency ω and the functions $L_{j'}^{(j-j')}(x)$ denoting the associated Laguerre polynomials. When $\beta=0$, this expression reduces to that employed for Franck–Condon analyses.¹² In the non-Condon case ($\beta \neq 0$), Eq. (3) can be used to investigate anharmonic oscillators (e.g., Morse) by exploiting the same perturbative corrections introduced in our previous work,^{4,5}

$$\begin{aligned} \alpha &= \alpha_0(1 - \xi v), \quad \alpha' = \alpha'_0(1 - \xi' v'), \\ \Delta &= \Delta_0 - \eta v + \eta' v', \end{aligned} \quad (4)$$

where a derivation of parameters $\xi(\xi')$ and $\eta(\eta')$ has been documented in Ref. 12 and their implications have been dis-

cussed in Refs. 4 and 5. In brief, $\xi(\xi')$ and $\eta(\eta')$ represent first-order corrections to the width (i.e., concavity) and coordinate origin, respectively, for the harmonic oscillators embodied in Eq. (3), thereby allowing the ensuing calculation of transition matrix elements to reproduce the classical turning points of a true Morse potential. As a practical demonstration of the method outlined above, our previous study of the $S_2O \tilde{C} \rightarrow \tilde{X}$ emission spectrum has been refined by going beyond the Condon approximation. The algebraic Hamiltonians used to describe the vibrational eigenstates of the \tilde{X}^1A' and \tilde{C}^1A' manifolds were parametrized in a manner identical to that described in Ref. 5. More specifically, the ground electronic state was found to exhibit essentially “local” or uncoupled dynamics while successful modeling of the electronically-excited \tilde{C} state necessitated the explicit

TABLE I. Perturbative and structural parameters employed for non-Condon analyses of vibronically-resolved $S_2O \tilde{C}^1A' \rightarrow \tilde{X}^1A'$ transition intensities are compiled for each local vibrational degree of freedom. The quantities α_0 denote inverse oscillator length (concavity), Δ_0 refer to translational displacements accompanying $\pi^* \leftarrow \pi$ electronic excitation, and β characterize the dependence of transition dipole moment on nuclear coordinates. The parameters ξ and η represent first-order perturbative corrections for concavity and displacement, respectively.

Parameter	S–O stretch	S–S stretch	S–S–O bend
\tilde{C}^1A' surface			
α_0 (\AA^{-1})	18.95	16.2	9.35
ξ	0.0044	0.015	0.0024
η (\AA)	0.004	0.002	–0.002
\tilde{X}^1A' surface			
α_0 (\AA^{-1})	18.95	15.96	10.99
ξ	0.0044	0.0035	0.00189
η (\AA)	0.0	0.003	0.0088
Translational displacement			
Δ_0 (\AA)	0.028	0.288	0.085
Non-Condon parameter			
β (\AA^{-1})	–2.5	–4.5	0.0

inclusion of substantial off-diagonal anharmonicities that lead to pronounced mixing of local vibrational character. Further refinement of these algebraic Hamiltonians will be addressed in a future publication;⁶ however, Table I contains a compilation of the new structural and perturbative parameters deduced from the present non-Condon analyses.

The quantities displayed in Table I are in good accord with those obtained from our prior Franck–Condon treatment (in Table IV of Ref. 5 a misprint occurred leading to interchange of the \tilde{X} and \tilde{C} labels), the only notable exceptions being found in the case of perturbative parameters. Potential concavities have remained unchanged except for a 2.5% increase along the S–S coordinate (which is affected most directly by the inclusion of non-Condon effects) while translational displacements have been modified by less than 0.015 \AA . Aside from providing an indication for error limits, the small magnitude of these differences suggests a \tilde{C}^1A' equilibrium geometry that remains essentially identical to that reported in our previous work.⁵ In particular, the $\tilde{C}^1A' \leftarrow \tilde{X}^1A'$ transition leads to elongation of the S–O and S–S bonds from 1.459 to 1.487 \AA and from 1.8845 to 2.173 \AA , respectively, while the S–S–O angle changes from the ground state value of 118.08° to either 105.2° or 110.5° depending upon the (indeterminate) sign of Δ_0^{SSO} (see Ref. 5 for further details). Specific results obtained for S_2O are displayed in Fig. 1 where predictions derived from non-Condon and Franck–Condon analyses are compared with measured vibronic intensities for the (a) 2_0^1 and (b) 2_0^3 progressions. Clearly, inclusion of non-Condon effects greatly improves the quality of theoretical simulations, especially for resonances terminating on higher-lying vibrational levels of the \tilde{X}^1A' manifold. Global agreement (for a data set consisting of over 1000 observed vibronic transition intensities) is reached only when a nuclear dependence of the transition moment is introduced along both the S–O and S–S stretching coordinates, with the optimized values for the corre-

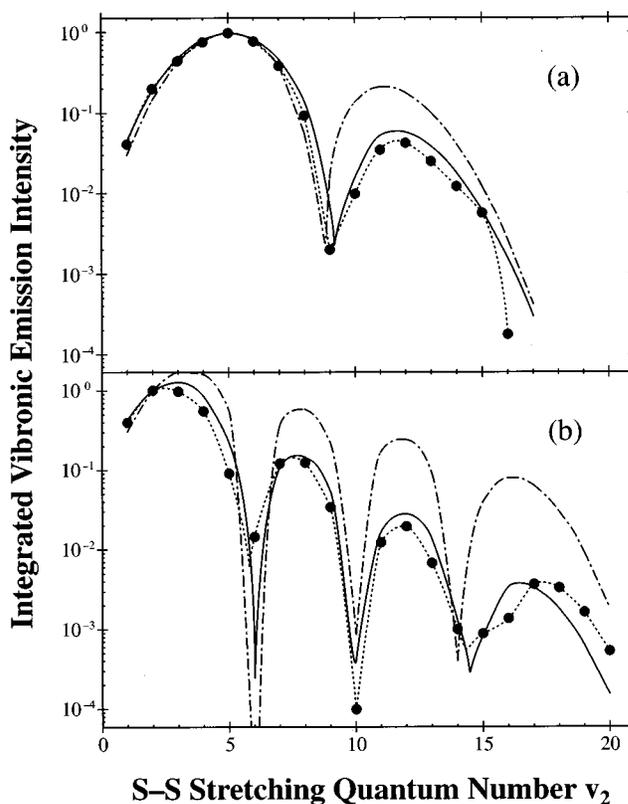


FIG. 1. A comparison of Franck–Condon and non-Condon algebraic analyses for dispersed fluorescence data acquired through excitation of the (a) 2_0^1 and (b) 2_0^3 bands in the $S_2O \tilde{C}^1A' \rightarrow \tilde{X}^1A'$ ($\pi^* \leftarrow \pi$) absorption system. The integrated spectral irradiance is shown on a logarithmic scale as a function of vibrational quantum number ν_2 (S–S stretching mode). Symbols connected with dotted lines represent experimental data while dash-dotted lines refer to Franck–Condon calculations and solid lines correspond to the non-Condon results.

sponding non-Condon parameters found (through manual iteration) to be given by $\beta_{SO} = -2.5 \text{\AA}^{-1}$ and $\beta_{SS} = -4.5 \text{\AA}^{-1}$. Rigorous estimates for the statistical uncertainties associated with these quantities, as well as those attributed to other structural and perturbative parameters, are precluded by the manual iteration procedures employed for their determination; however, it was noted that independent alteration of β_{SO} by $\sim 25\%$ or β_{SS} by $\sim 10\%$ markedly reduced the ability of theory to reproduce experimental observations.

Careful inspection of Eq. (3) reveals that the quantity $\gamma = \beta^2 / (\alpha'^2 + \alpha^2)$ provides an indication for the relative strength of the non-Condon effect. Non-Condon effects are absent for $\gamma = 0$ and substantial on the length scale of the oscillators for $\gamma \approx 1$. For the S–O stretching coordinate a modest γ value of 0.0087 is found, while the S–S stretching coordinate displays a much stronger effect characterized by $\gamma = 0.039$. The lack of quantitative non-Condon information for the S–S–O bending coordinate reflects the change in nuclear geometry accompanying the $\pi^* \leftarrow \pi$ electronic excitation, which mainly provides access to the S–S stretching coordinate. While additional information on the S–O stretching vibration follows from pronounced coupling of the local S–O and S–S stretching oscillators in the \tilde{C}^1A' state,^{4,5} the minute magnitude of mixing involving the bending vibration

precludes detailed investigation of the transition moment dependence along this coordinate.

The results discussed in this communication constitute a small portion of a global analysis for all observed $S_2O \tilde{C} \rightarrow \tilde{X}$ emission intensities, which previously had been interpreted within a Franck–Condon framework.⁵ A full set of non-Condon results will be presented in a later publication.⁶ The present work strengthens the conclusion that the combination of Lie algebraic methods for obtaining vibrational wave function information¹³ and explicit analytical formulas for the matrix elements of transition operators¹² provides a powerful technique for investigating molecular properties. This is especially true for studies that need to go beyond restrictions imposed by traditional (oftentimes qualitative) analyses of polyatomic intensities so as to incorporate the complicating effects found in real molecular systems (e.g., anharmonicity, dependence of transition moments on nuclear coordinates, etc.). To our knowledge, this study represents the first case for which non-Condon effects are modeled quantitatively in a bound-to-bound transition of a polyatomic molecule. Future publications will highlight further enhancements of the vibron model as a means of unraveling the intensity patterns found in vibronically-resolved electronic spectra, including extensions designed to address linear-to-linear, linear-to-bent, and bound-to-free transitions in triatomic molecules as well as analogous resonances in more complex species.

This work was supported in part by U.S. D.O.E. Grant No. DE-FG02-91ER40608 and the NSF Experimental Physical Chemistry Program. P.H.V. gratefully acknowledges the Dreyfus Foundation for a Camille Dreyfus Teacher-Scholar Award and The Packard Foundation for support through a Packard Fellowship for Science and Engineering.

- ¹J. Franck, *Trans. Faraday Soc.* **21**, 536 (1925); E. U. Condon, *Phys. Rev.* **32**, 858 (1928); G. Herzberg and E. Teller, *Z. Phys. Chem. Abt. B* **2**, 410 (1933); E. U. Condon, *Am. J. Phys.* **15**, 365 (1947).
- ²J. B. Coon, R. E. DeWames, and C. M. Loyd, *J. Mol. Spectrosc.* **8**, 285 (1962); D. C. Moule, in *Vibrational Structure in Electronic Spectra: The Poly-Dimensional Franck–Condon Method, Vibrational Spectra and Structure: A Series of Advances*, edited by J. R. Durig (Elsevier Scientific, Amsterdam, 1977), p. 228.
- ³For an extensive list of references see *J. Chem. Phys.* **111**, 5038 (1999).
- ⁴T. Müller, P. Dupré, P. H. Vaccaro, F. Pérez-Bernal, M. Ibrahim, and F. Iachello, *Chem. Phys. Lett.* **292**, 243 (1998).
- ⁵T. Müller, P. H. Vaccaro, F. Pérez-Bernal, and F. Iachello, *J. Chem. Phys.* **111**, 5038 (1999).
- ⁶T. Müller, P. H. Vaccaro, F. Pérez-Bernal, and F. Iachello (unpublished).
- ⁷A. Nitzan and J. Jortner, *J. Chem. Phys.* **56**, 3360 (1972); W. H. Henneker, W. Siebrand, and M. Z. Zgierski, *Chem. Phys. Lett.* **68**, 5 (1979); W. Siebrand and M. Z. Zgierski, *ibid.* **72**, 411 (1980); *J. Chem. Phys.* **72**, 1641 (1980).
- ⁸W. H. Henneker, W. Siebrand, and M. Z. Zgierski, *J. Chem. Phys.* **74**, 6560 (1981); H. M. Lu and J. B. Page, *ibid.* **88**, 3508 (1988); A. C. Albrecht, R. J. H. Clark, D. Opreescu, S. J. R. Owens, and C. Svendsen, *ibid.* **101**, 1890 (1994).
- ⁹S. Franzen, R. F. Goldstein, and S. G. Boxer, *J. Phys. Chem.* **97**, 3040 (1993).
- ¹⁰H. Goto, Y. Adachi, and T. Ikoma, *Phys. Rev. B* **22**, 782 (1980); Y. Tanimura and S. Mukamel, *J. Opt. Soc. Am. B* **10**, 2263 (1993).
- ¹¹V. Engel, R. Schinke, and V. Staemmler, *J. Chem. Phys.* **88**, 129 (1988); C. Woywod, M. Stengle, W. Domcke, H. Flöthmann, and R. Schinke, *ibid.* **88**, 129 (1997); T. Schröder, R. Schinke, M. Ehara, and K. Yamashita, *ibid.* **109**, 6641 (1998); A. Koch, E. F. van Dishoeck, and M. C. van Hemert, *Ber. Bunsenges. Phys. Chem.* **99**, 393 (1995); F. N. Dzegilenko, J. M. Bowman, and Y. Amatatsu, *Chem. Phys. Lett.* **264**, 24 (1997).
- ¹²F. Iachello and M. Ibrahim, *J. Phys. Chem. A* **102**, 9427 (1998).
- ¹³F. Iachello, *Chem. Phys. Lett.* **78**, 581 (1981); F. Iachello and R. D. Levine, *J. Chem. Phys.* **77**, 3046 (1982); O. S. van Roosmalen, A. E. L. Dieperink, and F. Iachello, *Chem. Phys. Lett.* **85**, 32 (1982); O. S. van Roosmalen, F. Iachello, R. D. Levine, and A. E. L. Dieperink, *J. Chem. Phys.* **79**, 2515 (1983).