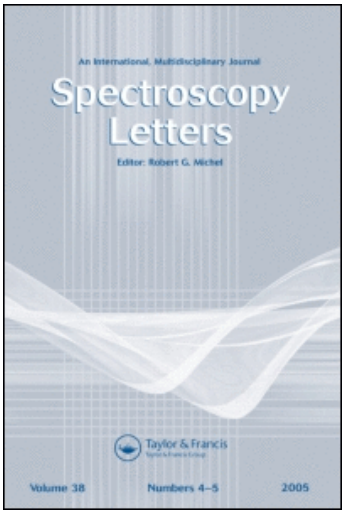

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LEVEL CROSSINGS IN INDO BENDING POTENTIALS FOR CO_2

KEY WORDS: INDO, CONFIGURATION INTERACTION

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Recently, Combs and Holloman have reported anomalous energy minima in approximate SCF calculations on bending modes in several small molecules.[1,2] The methods employed (CNDO/2 and INDO)[3] are currently in wide use and it would be helpful to have a clear view of the origin(s) of these anomalies. [As has been demonstrated,[2] reparameterization to remove these features creates more serious problems than that for which the remedy was derived.] We were particularly concerned as recent studies have shown that INDO wavefunctions, when properly handled, provide a qualitatively correct description of the electronic charge distribution in selected diatomic molecules.[4] Further, these methods are extensively used for studies of molecular deformations.[5]

On examining the published curves for CO_2 and FNO_2, we noted what appeared to be discontinuities in the first derivative for the energy vs bond angle plots in the "barrier" region. This suggested that the single

determinatal wavefunction is, for some reason, inadequate at this level of approximation. We report herein results which support this point of view. We have developed in our laboratory the program INDOCI2 which, subsequent to the SCF calculation, generates a set of configuration interaction wavefunctions built from all doubly excited configurations involving pairwise excitation, e.g., for the ground state

$$\Psi^0_{CI} = \Phi_{SCF} + \sum_{i,k} C_{ik} \Phi^{kk}_{ii} \tag{1}$$

Also available are the SCF configuration energies calculated as

$$\langle \Phi^{kk}_{ii} | \hat{H} | \Phi^{kk}_{ii} \rangle - E^0 = 2(\varepsilon_k - \varepsilon_i) - 4J_{ik} + 2K_{ik} + J_{kk} + J_{ii} \tag{2}$$

Using this method we have re-examined the bending coordinate for CO_2 (r_{CO} = 1.1612 Å) over the range $60° \leq \Theta \leq 180°$.

It is important to monitor orbital occupation as a function of bending. In the region 95°-180°, INDO calculations give the ordering under the point group $D_{\infty h}$

$$3a_{1g}{}^2(3a_1^2),\ 2a_{2u}{}^2(2b_1^2),\ 1e_{1u}{}^4(1b_2^2, 4a_1^2),\ 4a_{1g}{}^2(5a_1^2),$$

$$3a_{2u}{}^2(3b_1^2),\ 1e_{1g}{}^4(1a_2^2, 3b_1^2);\ 2e_{1u}(6a_1, 2b_2)\ .$$

The parenthesized specifications correspond to the symmetry designations appropriate for $\Theta \neq 180°$ under the point group C_{2v}. In our calculations we found that the ground state (SCF) electronic configuration was $(\cdots 1a_2^2 3b_1^2)$ in the region 95°-180°, but changed to $(\cdots 1a_2^2 6a_1^2)$ at smaller angles. Clearly, then, the aforementioned discontinuity in slope arises via level crossing (see Fig. 1). Inspection of the behavior of the relevant configuration energies (before CI) reveals curve discontinuities in the region of the maximum. This arises from the use of ground state SCF orbitals to calculate their energies (eqn. 2). The relief of these dis-

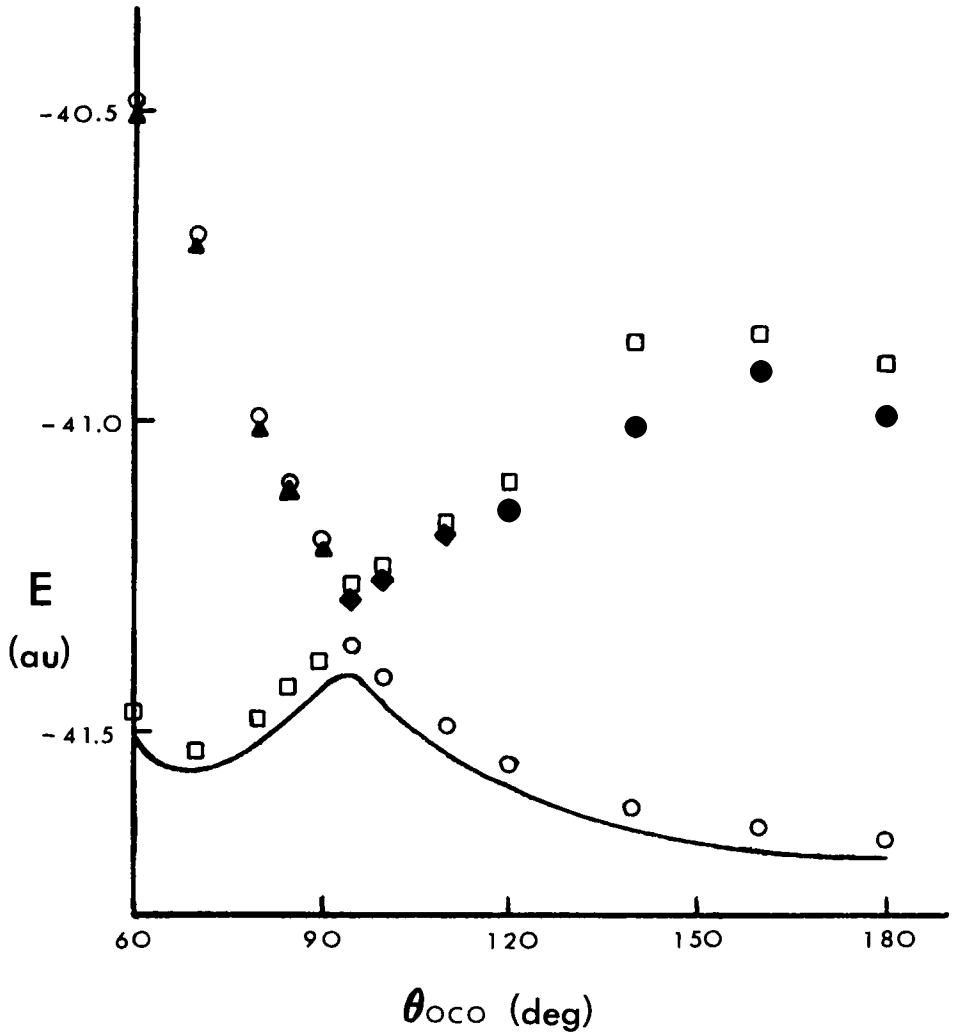

FIG.

THE TOTAL ENERGY OF SELECTED ELECTRONIC STATES FOR CO_2 VERSUS THE OCO ANGLE. (□) (·····$1a_2^2$ $6a_1^2$) BEFORE CI; (◆) (·····$1a_2^2$ $6a_1^2$) AFTER CI; (○) (····· $1a_2^2$ $3b_1^2$) BEFORE CI; (▲) (·····$1a_2^2$ $3b_1^2$) AFTER CI; (—) Ψ^0 (AFTER CI).

continuities is not apparent after CI. This is due in part to the plethora of avoided crossings in this region. Several configurations not shown, in particular $(\cdots 4b_1^2\ 6a_1^2)$, make strong contributions in this regard. The important feature to note, however, is that the slope discontinuity for the ground state wavefunction has been removed by this procedure.

It is possible that more extensive CI might eliminate the (presumably) spurious maximum altogether, but this begs the main questions regarding INDO calculations. The recent non-empirical SCF-MO studies of CO_2 by Davidson, et. al., show no level crossing in the region 90°-180°.[6] This is completely analogous to the results for FNO_2.[7] Clearly, then, spurious level crossing arises as a consequence of the approximations inherent in CNDO and INDO. The recent INDO studies of allene deformation[5] show a local minimum which, in view of the results reported herein, is suspect. It seems clear that these NDO methods, while suitable for small molecular deformations, can lead to erroneous conclusions unless employed judiciously.

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