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Correlation Between Energy Transfer Rate and Atomization Energy of Some Trinitro Aromatic Explosive Molecules

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An assumptive theoretical relationship is suggested to describe the property of molecular atomization energy and energy transfer rate in the initiation of explosions. To investigate the relationship between atomization energy and energy transfer rate, the number of doorway modes of explosives is estimated by the theory of Dlott and Fayer in which the rate is proportional to the number of normal mode vibrations. It was evaluated frequencies of normal mode vibrations of eight molecules by means of density functional theory (DFT) at the b3p86/6-31G(d,p) level. It is found that the number of doorway modes shows a linear correlation to the atomization energies of the molecules, which were also calculated by means of the same method. A mechanism of this correlation is discussed. It is also noted that in those explosives with similar molecular structure and molecular weight, the correlation between the atomization energy and the number of doorway modes is higher.

Key words: Secondary explosive, Atomization energy, Normal mode vibration, Doorway region

I. INTRODUCTION

Energetic materials have been investigated over many years. In order to understand how shock waves and impact can initiate the rapid exothermic reactions that lead to detonation in explosive solids, most of the previous studies have focused mainly on ground electronic state in the condensed phase [1-4]. However, this does not expose the difference between the intramolecular and intermolecular behaviors and the fundamental properties of these molecules [5]. To understand the properties of energetic materials at a fundamental level, an elucidation of their molecular behavior is essential. Gas phase studies of these energetic materials can reveal the behavior of such molecular species.

The molecular decomposition of high explosives has been regarded as an important step in explosive detonation kinetics. But most of explosive is crystal, and shock or impact initiation of explosives is quite a complicated process. Under a mechanical excitation, the mechanical energy is eventually dissipated into the bath of phonon. Before detonation, bonds of molecules in the crystal must be broken to initiate chemical reactions and lead to the decomposition of molecules. Therefore, the initial energy must be diverted and deposited to molecular vibrations again [6]. It is well known that typical phonon generally have frequencies less than 200 cm^{-1}, whereas molecular vibrations relevant to bond breaking have frequencies greater than 1000 cm^{-1}. Thus phonon energy must be converted to intramolecular higher vibrations by multiphonon up pumping [7].

In 1990, Dlott and Fayer derived a simple expression for the phonon-vibration energy transfer rate in which the rate is proportional to the number of normal mode vibrations [8]. Fried and Ruggiero have estimated the phonon up-conversion rates for several explosives such as RDX, picric acid, TATB, styphnic acid, beta-HMX, gamma-HMX, and pb styhnate, and they showed that the energy transfer rates at the vibrational frequency of ω=425 cm^{-1} are linearly correlated to the impact sensitivities derived from drop hammer tests [7]. McNesby and Coffey also studied the impact sensitivity as a function of the transfer rate into the phonon mode structure and estimated the phonon up-conversion rates for several explosives such as RDX, NQ, TATB, TNT, beta-HMX, gamma-HMX, and PETN [9]. Ye *et al.* estimated frequencies of normal mode vibrations of PETN, β-HMX, RDX, Tetryl, TNT, FOX-7, m-DNB, ANTA, PN, NQ, NTO, and DMN by means of DFT calculations at the B3LYP/6-31G(d) level [6]. They also found that the number of doorway modes shows a strong correlation with impact sensitivities obtained by drop hammer tests. These previous works indicated that the expression for the phonon-vibration energy transfer rate derived by Dlott and Fayer was reliable.

Given the complexity of detonation chemistry of high explosives, it is not surprising to see that the energy transfer alone is not enough to capture high explosive′s detonation process, which is likely to be influenced by other energy sources and reaction paths. One such source is the atomization energy of the gas phase unimolecule in this study. We did not employ crystallographic structures and only considered the explosive unimolecule. In this work, the atomization energy is a promising indicator for predicting high explosive energy transfer rate. As mentioned above, it is clear that

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the energy transfer rate show that a sizable amount of phonon energy must be converted to the molecular internal higher vibrations by multiphonon up pumping in the detonation process, which elucidates why the energy transfer rate shows the some properties of explosive molecular structure to some extent. The number of doorway modes could explain some properties of the molecular structure, and it ought to be correlated to the atomization energy of this molecule. Secondly, the detonation reaction of explosives is the end result of a chain of events. Phonon energy must be up converted to vibron, and then vibrational energy must be localized in a particular molecule. Finally, as Fried and Ruggiero argued, localized vibrational energy in a molecule must be channeled into a reaction coordinate. Reaction occurs when the excitation of the reaction coordinate exceeds the dissociation energy. It is clear that the atomization energy of the molecule must play an important role in determining the dissociation of molecule. In order to understand the properties of explosive molecules in the detonation process, an assumptive theoretical relationship is suggested to describe the property of molecular energy transfer and atomization energy in the explosive process in the present paper, which is that energy transfer rates are proportional to the atomization energy of the molecule to some extent. So according to the expression for the phonon-vibration energy transfer rate derived by Dlott and Fayer, we carried out a systematic study of the relationship between atomization energies and energy transfer rate of eight high explosive molecules using density functional theory (DFT). It was found that the number of doorway modes shows a linear correlation to the atomization energies.

II. COMPUTATIONAL METHODS

A. Theory of calculation of the energy transfer rate

In classical theory of detonation, the thermodynamic state of the system is described by the Chapman-Jouguet (C-J) model [10-14]. But this successful theory does not provide the insight into the molecular level events occurring in the solid behind the shock front. During the 1980s, several authors attempted to calculate the rate of vibrational up-pumping [15,16], but they did not obtain what they wanted. In contrast, during the 1990s, experimental studies of the flow of vibrational energy into or out of large organic molecular solids showed that these processes were more efficient than previously predicted [8,17]. According to Ref.[18], it was shown that the relatively low-frequency, large-amplitude vibrations in large molecules can be excited readily via a low order anharmonic coupling process, typically two-phonon absorption. Once these vibrations in large molecules have been excited, a variety of efficient intramolecular vibrational redistribution (IVR) processes come into play, redistributing energy from the

excited doorway modes to the other internal vibrations [18].

Dlott and Fayer studied multiphonon up conversion processes [8,18]. They assumed that the most efficient route for doorway mode pumping is absorption of a pair of phonons whose frequencies are about one half of the doorway mode frequency ν and they derived a simple expression for the phonon-vibron energy transfer rate.

In their theory, doorway modes are molecular vibrations located just above the phonon cutoff frequency $\nu_{\max}$. The large molecules being considered have doorway modes whose frequency ν is in the range of $\nu_{\max}$-$2\nu_{\max}$. Therefore doorway mode pumping in these systems occurs via simultaneous absorption of two phonons. Absorption of further phonons transfers energy into higher modes until the IVR threshold energy (ΔE_{IVR}) is reached and IVR randomizes the excitation. If doorway mode pumping is much more efficient than energy transfer from doorway modes to other low frequency vibrations, then doorway mode overtones are pumped by the shock up to ΔE_{IVR}. In addition, when molecule has very low-frequency vibrational modes which lie below $\nu_{\max}$, these vibrations do not act as doorway modes because they are amalgamated with the phonons. Amalgamated vibrations behave much like phonons in that they will be directly excited by the shock.

In their theory, the dominant mechanism for up-pumping is caused by a cubic term of anharmonic potential [18,19]:

$$V^{(3)} = \frac{1}{3!} \sum_{\Psi} \left. \frac{\partial^3 V(\{\Psi\})}{\partial \Psi_1 \partial \Psi_2 \partial \Psi_3} \right|_{\Psi_0} \Psi_1 \Psi_2 \Psi_3 \qquad (1)$$

here $V(\{\Psi\})$ is the potential energy surface for the molecular crystal with a set of normal coordinates $\{\Psi\}$, and the partial derivative is evaluated at the equilibrium position $\{\Psi\}_0$. The temperature and specific-volume dependent rate are constant for energy transfer between a doorway mode of frequency ν, and a pair of phonon whose frequencies lie near $\nu/2$ is k. k is the energy transfer parameter that characterizes the rate of energy transfer from external to doorway mode, and can be calculated by using the following relation [8,19-22]:

$$\begin{aligned} k_{2\mathrm{ph}\to\mathrm{vib}} = & \frac{36\pi^2}{\hbar} \langle V^{(3)}(V) \rangle^2 \rho^2(\nu) \cdot \\ & [n_{\mathrm{ph}}(T,V) - n_{\mathrm{vib}}(T,V)] \end{aligned} \qquad (2)$$

here $\langle V^{(3)}(V) \rangle$ denotes the specific volume-dependent matrix element of the operator in Eq.(1), the value of $\langle V^{(3)}(V) \rangle$ can be determined empirically, or by direct calculation using model intramolecular potential [21,22]. $\rho^2(\nu)$ is the two-phonon density of states at the doorway mode frequency ν. The product of the matrix element and the two-phonon density of states in Eq.(2) can be determined experimentally by measuring

$\tau_1(0)$, the lifetime of the doorway mode at temperature $T=0$ K.

Also, $n_{\mathrm{ph}}(T,V)$ refers to the Planck occupation factor of phonons of frequency $\omega=\nu/2$, and $n_{\mathrm{vib}}(T,V)$ is the Planck occupation factor at the doorway mode frequency ν. At the temperatures being considered, the Planck occupation factors $n_\nu(T)$ can be approximated as: $k_{\mathrm{B}}T/\hbar\nu$. Therefore, the up-pumping rate is proportional to the difference in quasitemperatures and the time dependence of the phonon and vibrational quasitemperatures can be described [8,18]. Then the value of $K(V)$ can be calculated by the following:

$$\kappa = \frac{j\hbar\nu}{\tau_1(0)\theta_e} \tag{3}$$

where j is the number of vibron states in the doorway region, ν is the vibrational frequency of the doorway state, θ_e is the equivalence temperature, at which the rate of up-pumping into the doorway mode is equal to the low temperature rate of relaxation by the two phonon emission, $\tau_1(0)$ is the lifetime of doorway mode at temperature $T=0$ K. θ_e is defined by the relation $n_{\nu/2}(\theta_e)$-$n_\nu(\theta_e)=1$. Here $n_\nu(\theta_e)$ is the occupation number of phonon at frequency ν and temperature θ. For $\nu=200$ cm^{-1}, $\theta_e=300$ K. Therefore, based on Eq.(3), the value of κ can be evaluated by knowing $\tau_1(0)$, the lifetime of doorway mode at temperature $T=0$ K, and j, the number of doorway modes.

The lifetime for phonon and vibron of explosives at $T=0$ K can be estimated by the analysis of the Raman line width [6,23,24]. According to Ye *et al.* work, the value of $\tau_1(0)$ was not very different between a rigid molecule crystal and a floppy molecular explosive with low vibrational frequencies [6]. Also, Tokmakoff *et al.* has pointed out that a constant value of $\tau_1(0)$ may be used for the rough estimation of the energy transfer rate for many secondary explosives [18]. Therefore, the value of $\tau_1(0)$ is assumed to be constant for all the explosives investigated in the present work. With this assumption the overall relaxation rate of vibron is directly proportional to a value of j.

B. Theory of calculation of the atomization energy

The atomization energy (E_a) is the energy change for the process: gas-phase molecule→gas-phase atoms. In order to calculate E_a one calculates the molecular electronic energy E at the equilibrium geometry, calculates the ground-state energy of each atom in a molecule using the same method and basis set used in molecular calculation, and takes the difference between the total atomic energies and molecular energy. For molecule $C_xH_yN_zO_k$ we have calculated the atomization energy E_a with the definition:

$$E_a(C_xH_yN_zO_k) = xE(C) + yE(H) + zE(N) + kE(O) - E(C_xH_yN_zO_k) \tag{4}$$

In this work, we use this value and define three doorway regions the same as the Ye *et al.* [6]. These three regions are defined as Region B(200-700 cm^{-1}), Region X(200-600 cm^{-1}), and Region Δ(200-500 cm^{-1}). The number of vibrational states, j, is calculated by the direct counting method and we have studied all the overtones and combination bands of the fundamental vibrations in the doorway region without including the overtones and combination bands of fundamentals that have frequencies less than 200 cm^{-1}. It is noted that our calculation did not include the combination bands such as $m\omega_1+n\omega_2$ ($n,m\geq2$). The numbers of vibrational states in the doorway regions of these several secondary explosives were estimated using density functional theory [25,26], b3p86 [27-29], and the 6-31G(d,p) basis set [30]. The atomization energy of every molecule was calculated using the same method. The calculation was performed using the Gaussian 98 system [31]. Therefore, vibrational relaxation rates of these explosives were estimated by the direct counting method and compared with the atomization energy. The molecules studied are picric acid ($C_6H_3N_3O_7$, 2,4,6-trinitrophenol), TBN ($C_7H_2N_4O_6$, 2,4,6-trinitrobenzonitrile), TNT ($C_7H_5N_3O_6$, 2,4,6-trinitrotoluene), 2,4,6-trinitro-m-cresol ($C_7H_5N_3O_7$), 2,4,6-trinitro-benzaldehyde ($C_7H_3N_3O_7$), 2,4,6-trinitro-benzaldoxime ($C_7H_4N_4O_7$), 2,4,6-trinitro-triphenol ($C_6H_3N_3O_9$), and TATNB ($C_6N_{12}O_6$ 1,3,5-triazdo-2,4,6-trinitrobenzene). The normal mode and energy analysis for each structure resulted in six zero frequencies, and no imaginary frequencies for the remaining $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. We have computed the ground state energies of each molecule and atom, in particular for C, H, N, and O the electronic states are $^3P_0$, $^2S_{1/2}$, $^4S_{1/2}$, and $^3P_2$, respectively.

III. RESULTS AND DISCUSSION

The values of j in different regions and E_a of every molecule are listed in Table I. The values of j for the Region B are plotted as a function of the atomization energy of explosive molecules in Fig.1(a). It can be seen that the j-number is linearly correlated to the atomization energy of explosive molecules. The correlation function is given by Eq.(5).

$$j = -128.752 + 46.886E_a \tag{5}$$

The linear correlation coefficient R is 0.978. The correlation for this series between the value of j and the atomization energy of explosive molecules is good.

The values of j for the Region X and Region Δ are plotted as a function of the atomization energy in Fig.1 (b) and (c). The linear regression R is 0.971 and 0.938 in

TABLE I The number of doorway modes and atomization energy

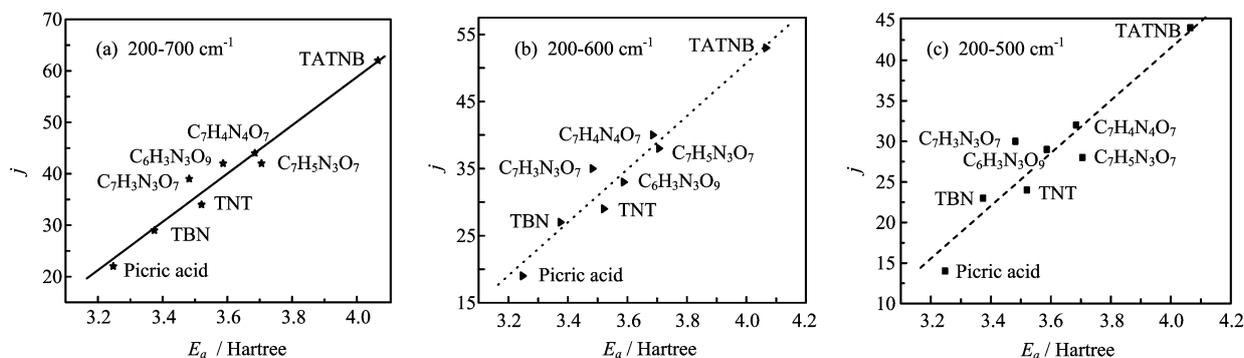| Explosives	E_a/Hartree	Doorway region			Molecular weight	Number group
		200-500 cm^{-1}	200-600 cm^{-1}	200-700 cm^{-1}		
Picric acid	3.247101	14	19	22	229	1-OH
TBN	3.374021	23	27	29	238	1-CN
TNT	3.520026	24	29	34	227	1-CH$_3$
C$_7$H$_5$N$_3$O$_7$	3.705565	28	38	42	243	1-OH, 1-CH$_3$
C$_7$H$_3$N$_3$O$_7$	3.482035	30	35	39	241	1-CHO
C$_7$H$_4$N$_4$O$_7$	3.684506	32	40	44	256	1-CHNOH
C$_6$H$_3$N$_3$O$_9$	3.58696	29	33	42	261	3-OH
TATNB	4.065231	44	53	62	348	3-N$_3$

FIG. 1 The number of vibrational states in the doorway region j of explosive molecules as a function of atomization energy.

Fig.1 (b) and (c) respectively. The correlation functions are given in Fig.1 (b) and (c) by Eq.(6) and Eq.(7), respectively.

$$j = -107.662 + 39.605 E_a \qquad (6)$$
$$j = -88.414 + 32.489 E_a \qquad (7)$$

The correlation between j-number and the atomization energy of explosive molecules for Region X and Region Δ shows similar tendencies with the ones in Region B. The scatters of these two plots are larger than that in Region B. This may be due to the number of vibrations in Region B being larger than that in the other two regions, thus the deviation due to doorway modes is smaller. So, for Region B, the correlation between the value of j and the atomization energy of explosive molecule is better than the other ones.

Our study shows that in those molecules having similar molecular structure and similar molecular weight, the correlation between the atomization energy and the number of doorway modes is very high. After the investigation of the deviation of every molecule in Fig.1(a), we found that the value of deviation is related to the group of trinitroamine molecules of explosives. It is clear that the H atom of the phenyl is replaced by some other groups in every molecule. The numbers of the group of each molecule are listed in Table I. The deviation for molecules with CHO group is larger. On

the other hand, the deviation from the symmetrical molecules (C$_6$N$_{12}$O$_6$ and C$_6$H$_3$N$_3$O$_9$) is almost equal to zero. So, in Fig.1(a), there is a good correlation between the j-number and the atomization energy of explosive molecules, except for C$_7$H$_3$N$_3$O$_7$. It is may be due to that this molecular structures are different from the others' and its vibrational frequencies is related to CHO group vibration in the doorway modes. For C$_7$H$_3$N$_3$O$_7$, related to the CHO group, the dominating vibration frequencies ν are 212, 432, 480, and 689 cm^{-1} in the doorway modes. In addition, our study shows that in these energetic materials with similar molecular weight, the correlation between the atomization energy and the number of doorway modes is higher. The molecular weight of every molecule in our study is also listed in Table I.

In order to investigate the accuracy of our calculation, a comparison of the calculated and observed vibrational transitions for TNT is listed in Table II. The maximal value of relative error is equal to 0.092, meaning that the calculation of vibrational frequencies is reliable in the present work.

IV. CONCLUSION

We evaluated frequencies of normal mode vibrations of unimolecules which are picric acid, TBN, TNT,

TABLE II Comparison of calculated and experimental vibrational frequencies for TNT

Exp.[32]	DFT	Absolute error	Relative error
1349	1422	27	0.020
1559	1702	143	0.092
2898	3066	168	0.058
3107	3140	33	0.011

2,4,6-trinitro-m-cresol, 2,4,6-trinitro-benzaldehyde, 2,4,6-trinitro-benzaldoxime, 2,4,6-trinitro-triphenol, and TATNB by means of density functional theory calculations at the b3p86/6-31G(d,p) level and estimated the number of doorway modes in three regions (200-700, 200-600, and 200-500 cm^{-1}) by the direct counting method. In this work, the value of the lifetime of vibron states at $T=0$ K, $\tau_1(0)$, is assumed to be constant for all the explosives. Based on this assumption, it can be predicted that the energy transfer rates are directly proportional to the number of vibron states in the doorway region and that the energy transfer rates are linearly correlated to the atomization energy in the secondary explosives that have similar molecular structure and similar molecular weight. Our results suggest that there is a strong correlation between energy transfer rate and the atomization energy of molecules in the explosive process. These results could help us gain insight into the properties of explosive molecules in their explosive process. This relationship needs be confirmed through the study of more systematic explosive materials.

V. ACKNOWLEDGMENTS

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