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Emission spectra and stimulated emission characteristics of $[N_2]_2$——N_2 molecular dimer

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Abstract It has been proved by *ab initio* calculation and theoretical analysis that there exist $[N_2]_2$——N_2 molecular dimers with D_{2h} symmetry group, and there also exists an electric dipole excimer-like transition $a^1B_{2g}\rightarrow a^1B_{3u}$. The theoretical spectra accord with the experimental results for transition $a^1B_{2g}\rightarrow a^1B_{3u}$. The stimulated emission characteristic of N_2 molecular dimer was researched through the microwave excited highly pure nitrogen and the method of amplified spontaneous emission. The experimental results show that N_2 molecular dimer has stimulated emission characteristics when the microwave power is more than 100 W and the N_2 pressure is in the range from 260 Pa to 2200 Pa.

Keywords: *ab initio*, potential energy curve, excimer-like molecule, oscillator strength, gain.

The weak interaction $[N_2]_2$——N_2 molecular dimer ——in the intermediate and long range van der Waals region has long been studied, and a number of theoretical[1—5] and experimental[6,7] researches about N_2 molecular dimer have been carried out for a long time. The major studies on N_2 molecular dimer have been made with focus on the point that the distance (R) between two N_2 molecular dimers is more than 0.3 nm. However, few reports have appeared on the emission spectra and stimulated emission characteristics of the strong interaction of N_2 molecular dimers in the short range of $0.12\text{ nm} < R < 0.3\text{ nm}$. The strongly interactive N_2 molecular dimers can be obtained through collision interaction between N_2, or excited N_2 produced by use of some exciting conditions, such as the strongly interactive N_2 molecular dimers produced in fast discharge at high temperature. In 1968, Tinti and Robinson[8] observed a blue-shifted side band near the 337.12 nm peak of N_2 by X-ray exciting rare gas-doped N_2 gas at low temperatures, the energy for this blue-shifted bands is higher than that from transition $N_2(C^3\Pi_g)\rightarrow N_2(B^3\Pi_u)(\Delta V = 0)$. At that time, they could not exactly characterize these spectra. The study of strongly interactive N_2 molecular dimers with $R < 0.3$ nm is reported in this paper. The geometrical structure for N_2 molecular dimer is firstly confirmed theoretically by calculating the potential energy curves of N_2 molecular dimers with different symmetry groups in the range of $0.13\text{ nm} < R < 0.25\text{ nm}$, then the possible bound-free and bound-bound electric dipole transitions of N_2 molecular dimers with confirmed symmetry group are researched by the *ab intio* method. The emission spectra and stimulated emission characteristic of N_2 molecular dimer are studied by microwave excited highly pure nitrogen to produce N_2 molecular dimers experimentally.

1 Theoretical calculation of emission spectra for N_2 molecular dimer

1.1 Theoretical model

Since the Hamiltonian for a molecular system is very complex, its Schrödinger equation is impossible to be resolved accurately, so different approximate methods must be introduced to resolve the Schrödinger equation of a molecular system. The *ab initio* calculation is an approximate method often used presently. The *ab initio* method is such that Schrödinger equation for a molecular system can be simplified as the following HF equations[9] by use of three basic approximations, namely the single electron approximation, the Born-Openheimer approximation and the non-relativistic approximation:

$$\hat{F}_i \phi_i(1) = \varepsilon_i \phi_i(1), \tag{1}$$

$$\hat{F}_i(1) = \hat{h}(1) + \sum (\hat{J}_j(1) - \hat{K}_j(1)), \tag{2}$$

$$\hat{J}_j(1)\varphi_i(1) = \left[\int \varphi_j^*(2)\hat{g}_{12}\varphi_j(2)d\tau_2 \right]\varphi_i(1), \tag{3}$$

$$\hat{K}_j(1)\varphi_i(1) = \left[\delta(m_{s_i} m_{s_j}) \int \varphi_j(2)\hat{g}_{12}\varphi_i(2)d\tau_2 \right]\varphi_i(1), \tag{4}$$

where $\hat{F}_i(1)$ is the Hartree-Fock operator, $\hat{h}(1)$ is the single electron operator, $\hat{J}_j(1)$ and $\hat{K}_j(1)$ are the Coulomb and exchange operators defined by formulae (3) and (4), respectively. Presently, the popular method for solving the HF equations is the Gaussian program; all calculations in this paper were achieved by the Gaussian-94 program. The Schrödinger equation for a molecular system can be resolved by using the HF equations approximately. But when the energy for a molecular system is computed by the HF equations, there will be errors between calculation and experimental results due to the HF equations being obtained through the three basic approximations. Therefore, the results of the HF calculation must be modified. The main errors for HF calculation come from the electronic correlation energy, the basis sets, and the relativistic effect.

Because basis sets and relativistic errors are much smaller than electronic correlation energy, and we can reduce the basis set errors to the lowest degree by choosing a suitable basis sets, while the relativistic energy is mainly contributed by the inner shell electrons of a molecular system, the study of N_2 molecular dimer in this work does not deal with the inner shell electrons, so only the correctoin of electronic correlation energy will be considered in the following calculation. Configuration interaction (CI), many-body perturbation theory (MBPT) and multiconfiguration self-consistent field (MCSCF) are often introduced to modify the electronic correlation energy. In this paper, N_2 molecular dimer is calculated by the HF method and basis set 6-31G, and the electronic correlation energy is corrected by CI.

1.2 Calculation and analysis of the geometrical structure and oscillator strength of N_2 molecular dimer

Since the geometrical structure of N_2 molecular dimer is unknown, it can be confirmed by calculating the potential energy curves of N_2 molecular dimer with different symmetry groups. Six possible geometrical structures, whose symmetry groups are $D_{\infty h}$, C_{2vx}, C_{2vz}, C_{2h}, D_{2d} and D_{2h} for the N_2 molecular dimer respectively, are considered. Because the distance (r) between two N nuclei in the same N_2 changes very little, so we only consider the potential energy curves denoting the energy of N_2 molecular dimer versus R in this paper.

Fig. 1(a) shows the theoretical calculation results of N_2 molecular dimer with C_{2vz} symmetry group (r = 0.123 nm), the ground state and a few lower excited states are repulsive for this symmetry group, while the potential energy curves for $D_{\infty h}$ and C_{2h} groups are the same as the potential energy curves of C_{2vz} group at r = 0.125 nm, their ground state and a few lower excited states are also repulsive. For D_{2h}, D_{2d} and C_{2vx} symmetry groups, the calculation results show that there are not only bound states, but also repulsive ones. Fig. 1(b) shows the potential energy curves of N_2 molecular dimer with D_{2h} group, where a^1B_{1g}, a^1A_u, a^1B_{2g}, a^1B_{3u} and X^1A_g states are bound, and a^1B_{3g} state repulsive.

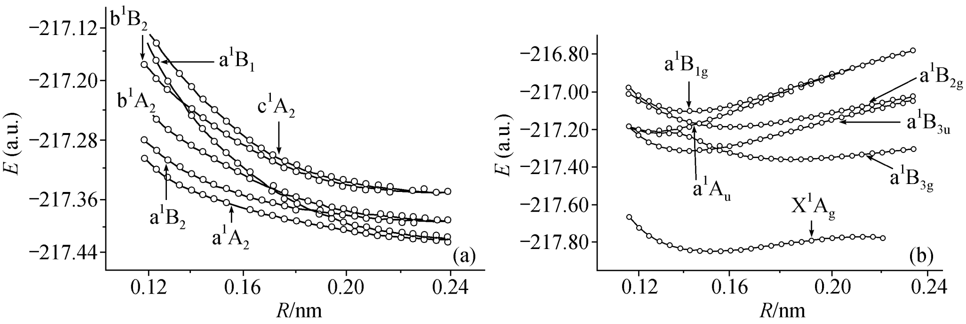

Fig. 1. Potential energy curves of N_2 molecular dimer. (a) C_{2vz} group, r = 0.125 nm; (b) D_{2h} group, r = 0.124 nm.

The above results were obtained by calculating the potential curves of N_2 molecular dimer belonging to the six possible symmetry groups. Because there are no minima in the potential curves of the ground and a few excited states for C_{2vz}, $D_{\infty h}$ and C_{2h} groups, there cannot exist N_2 molecular dimer with these three symmetry groups; while for D_{2h}, D_2 and C_{2vx} groups, there are not only bound potential energy curves, but also repulsive ones, so it is possible that there exists N_2 molecular dimer belonging to the three symmetry groups. But further calculation results indicate that there are electric dipole transitions only for the D_{2h} group. Therefore, the following is only about N_2 molecular dimer with D_{2h} group.

According to the selection rules of the electric dipole transition of multi-atom molecules, the possible electric dipole transitions are $a^1B_{1g} \rightarrow a^1A_u$, $a^1B_{1g} \rightarrow a^1B_{3u}$, $a^1B_{2g} \rightarrow a^1B_{3u}$ and $a^1B_{3u} \rightarrow X^1A_g$ in the states given in fig. 1(b), but the calculated oscillator strengths of transitions $a^1B_{1g} \rightarrow a^1A_u$,

a^1B_{1g}→a^1B_{3u} and a^1B_{3u}→X^1A_g are very small for different R values, only about 10^{-4} level, but the oscillator strengths of transition a^1B_{2g}→a^1B_{3u} are higher for some R values, so the following investigation is only concerned with transition a^1B_{2g}→a^1B_{3u}.

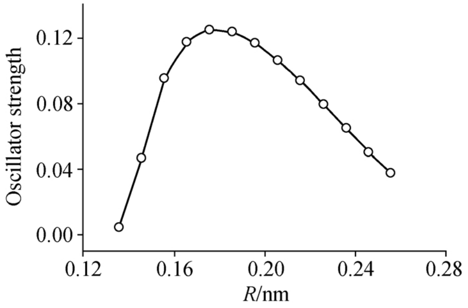

Fig. 2. The oscillator strength of transition a^1B_{2g}→ a^1B_{3u}.

Fig. 2 denotes the calculated oscillator strengths of transition a^1B_{2g}→a^1B_{3u} versus R. It can be seen from fig. 2 that the oscillator strength of transition a^1B_{2g}→a^1B_{3u} has a maximum when R is equal to 0.18 nm. Because the electric dipole moment increases with oscillator strength, this indicates that the transition probability for a^1B_{2g}→a^1B_{3u} is the maximum at R = 0.18 nm. In addition, the geometrical structures about a^1B_{2g} and a^1B_{2u} states are optimized by the *ab intio* method and 6-31G basis set. Table 1 gives the results optimized for the two states. E_0 (a.u.) is the energy of N_2 molecular dimer at equilibrium location, which is at 0.1756 nm for the a^1B_{2g} state, and 0.1559 nm for a^1B_{3u} one. It can be seen that a^1B_{3u} state intersects with $^1B_{3g}$ one at the equilibrium location (R_0, r_0), so when a^1B_{2g}→a^1B_{3u} transition occurs, an N_2 molecular dimer in a^1B_{3u} state will rapidly transit to a^1B_{3g} state, and then separate into two independent N_2 molecules, so there will be in fact no particle population in a^1B_{3u} state. This shows that a^1B_{2g}→a^1B_{3u} is an electric dipole excimer-like transition.

Table 1 The optimized results for a^1B_{2g} and a^1B_{3u} states

	r_0/nm	R_0/nm	E_0 (a.u.)
$^1B_{2g}$	0.1251	0.1766	−217.186
$^1B_{3u}$	0.1243	0.1559	−217.307

1.3 Theoretical calculation of emission spectra for N_2 molecular dimer

Here we only discuss the theoretical spectra of the excimer-like transition a^1B_{2g}→a^1B_{3u} for N_2 molecular dimer. The above calculation of potential energy curves only indicates the possible existence of N_2 molecular dimer with D_{2h} symmetry group. But the stability of each bound state must be confirmed by the normal vibrational frequencies of each state. According to quantum chemistry[10], a bound state is stable only when all the normal vibrational frequencies are positive; otherwise, it will be an unstable transition state.

The normal vibrational frequencies of a^1B_{2g} and a^1B_{3u} states were calculated by the *ab initio* method and 6-31G basis sets, the calculation results are shown in table 2. It can be seen that the six normal vibrational frequencies for state a^1B_{2g} are all positive, but for state a^1B_{3u} one negative and the others positive. So a^1B_{2g} is a stable state, and a^1B_{3u} an unstable transition one. This further proves that a^1B_{2g}→a^1B_{3u} is an excimer-like transition.

Table 2 The normal vibrational frequencies (ω/cm^{-1}) for a^1B_{2g} and a^1B_{3u} states

	$\omega(A_u)$	$\omega(B_{2u})$	$\omega(A_g)$	$\omega(B_{3g})$	$\omega(B_{1u})$	$\omega(A_g)$
$^1B_{2g}$	259.613	686.565	861.084	867.756	1168.182	1424.545
$^1B_{3u}$	600.427	−159.357	919.272	629.785	1192.273	1793.932

The previous calculations have given the electronic levels of a^1B_{2g} and a^1B_{3u} states, namely the potential energy curves. In order to calculate the emission spectra of $a^1B_{2g}\rightarrow a^1B_{3u}$ transition, the vibrational levels for a^1B_{2g} and a^1B_{3u} states must be calculated. The vibrational levels for a multi-atom molecule can be obtained by the following formula:

$$E_v(v_1v_2\cdots\cdots)=\sum_{k=1}^{n}(v_k+1/2)hv_k, \tag{5}$$

where $v_k=\omega_k\times c$ is the kth normal vibrational frequency of a molecule, v is the vibrational quantum number, and n is the number of normal vibrational frequencies for a molecule. Since the normal vibrational frequencies of a^1B_{2g} and a^1B_{3u} states have been calculated, it is easy to obtain the vibrational levels of these two states by use of formula (5). The negative normal vibrational frequencies are not considered during calculating the vibrational levels of a^1B_{3u} state.

First, the vibrational levels of a^1B_{2g} and a^1B_{3u} states are calculated by using formula (5) and their normal vibrational frequencies, and then the minimum electronic state energies and vibrational levels are used to calculate the electronic vibrational levels of a^1B_{2g} and a^1B_{3u}, and the emission spectra of transition $a^1B_{2g}\rightarrow a^1B_{3u}$ also are computed. Table 3 presents the calculated emission spectra of transition $a^1B_{2g}\rightarrow a^1B_{3u}$ according to the electronic vibrational levels of a^1B_{2g} and a^1B_{3u}. It can be seen that the emission spectra are located in the region from 320 nm to 440 nm.

Table 3 Theoretical spectra of N_2 molecular dimer

Transition	a^1B_{2g} (a.u.)	a^1B_{3u} (a.u.)	ΔE (a.u)	λ /nm
(002022)-(00011)	–217.14250	–217.28725	0.14475127	314.77
(111111)-(01101)	–217.14992	–217.28545	0.13552294	336.21
(055000)-(33030)	–217.13871	–217.26802	0.12931484	352.34
(010011)-(00011)	–217.15902	–217.28725	0.12822700	355.34
(020002)-(44000)	–217.15472	–217.27796	0.12323499	369.73
(200000)-(01100)	–217.17151	–217.29340	0.12188667	373.82
(002220)-(33030)	–217.14757	–217.26803	0.12045030	378.28
(110001)-(02002)	–217.16312	–217.27885	0.11573278	393.69
(220222)-(00044)	–217.13373	–217.24785	0.11412329	399.24
(200200)-(20220)	–217.16361	–217.27610	0.11249094	405.04
(000001)-(02220)	–217.16747	–217.27606	0.10858657	419.60
(010110)-(02022)	–217.16156	–217.26849	0.10693034	426.10
(001110)-(00222)	–217.16077	–217.26578	0.10501039	433.90

2 Experimental research on the emission spectra and stimulated characteristics of N_2 molecular dimer

2.1 Experimental observation fluorescence of N_2 molecular dimer and its mechanics analysis

Fig. 3 is an experimental setup used to observe the fluorescence of N_2 molceular dimer by microwave exciting highly pure N_2 (Here the purity of N_2 gas is 99.99%). The frequency of microwave source is 2.450 GHz, and the microwave source has continuous tunable power from 30

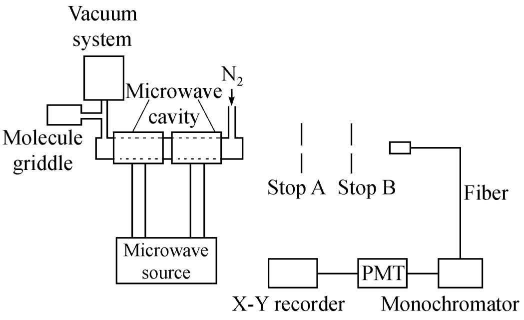

Fig. 3. Experimental setup.

W to 600 W. The microwave is guided to cavities A and B by a waveguide. A quartz tube with diameter of 1.8 cm passes through the center of cavities A and B, and highly pure N_2 is excited in the quartz tube. In the experiments, a 0.5-m monochromator was used, whose incident narrow slot and output one are 1.2 and 1.0 mm, respectively. When the vacuum degree in the discharge tube reaches 10^{-5} Pa, the discharge tube is filled with highly pure N_2, and the emission spectra from the discharge tube are observed. Fig. 4 shows the emission spectra observed when the microwave power was 300 W and the N_2 pressure was 600 Pa. It can be seen that there are also some new bands in the regions of ultraviolet and visible light besides the N_2 emission spectra. In addition, the new bands were also observed when the microwave power ranged from 50 W to 600 W, and the N_2 pressure from 100 Pa to 2600 Pa. These fluorescent spectra are located at blue-shifted bands of transition $N_2(C^3\Pi_g)\rightarrow N_2(B^3\Pi_u)(\Delta V = 0, \pm 1, \pm 2, \cdots)$, and they fit with the theoretical results we calculated, showing that the new fluorescent spectra come from N_2 molecular dimer excimer-like transition $a^1B_{2g}\rightarrow a^1B_{3u}$. The peak wavelengths of N_2 molecular dimer are 336.21 nm ($\Delta V = 0$), 352, 34 nm ($\Delta V = -1$), 355.33 nm ($\Delta V = -1$), 369.73 nm ($\Delta V = -2$), 373.82 nm ($\Delta V = -2$) and 378.28 nm ($\Delta V = -2$), respectively. These bands can be attributed to the following dynamics processes:

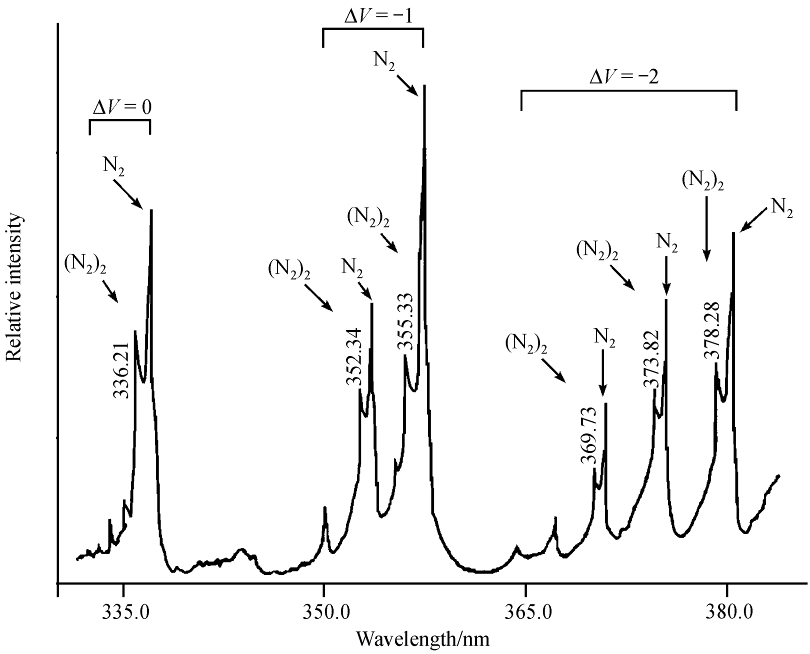

Fig. 4. The emission spectra of N_2 molecular dimer.

$$e + N_2(X^1\Sigma_g) \rightarrow N_2(C^3\Pi_u) + e \qquad \text{(microwave exciting)} \tag{6}$$

$$N_2(C^3\Pi_u) + N_2\,(X^1\Sigma_g) \rightarrow \{N_2(C^3\Pi_u){-}N_2(X^1\Sigma_g)\}^* \qquad (a^1B_{2g}\text{ state}) \tag{7}$$

$$\{N_2(C^3\Pi_u){-}N_2(X^1\Sigma_g)\}^* \rightarrow \{N_2\,(B^3\Pi_g){-}N_2(X^1\Sigma_g)\} + h\nu \qquad (a^1B_{3u}\text{ state + photon emission}) \tag{8}$$

$$\{N_2\,(B_3\Pi_g){-}N_2\,(X^1\Sigma_g)\} \rightarrow N_2^* + N_2^* \qquad (\text{relaxation to } a^1B_{3g}) \tag{9}$$

$$N_2^* + N_2^* \rightarrow N_2(X^1\Sigma_g) + N_2(X^1\Sigma_g) \rightarrow \qquad \text{(return to ground state)} \tag{10}$$

2.2 Research on the stimulated emission characteristics of N_2 molecular dimer

In order to explore the stimulated characteristics of N_2 molecular dimer experimentally, the small signal gain coefficients for 336.21 nm fluorescent band where N_2 molecular dimer has the maximum fluorescent emission intensity were measured by the amplified spontaneous emission method. When a full-reflective mirror for 336.21 nm is placed at the left end of the discharge tube as shown in fig. 3, a small signal gain coefficient at 336.21 nm can be measured. The reflective mirror used in the experiment has a reflectivity of 99.3% for 336.21 nm. The principle[11] for measuring small signal gain coefficient of active medium is described as follows:

$$G(\nu) = \frac{1}{l}\ln\left[\frac{I_{2l}/I_l - 1}{rT^2}\right], \tag{11}$$

where T is the transmittivity of the discharge tube's window, and r is the reflectivity of the reflective mirror, l is the length of the active region. The above equation can be used when the distance between the detector and active region $D \geqslant 10l$ (in this experiment, $l < 12$ cm, $D > 150$ cm).

The change of small signal gain coefficient G_0 varying with microwave power and N_2 pressure is studied for N_2 molecular dimer according to formula (11). Fig. 5(a) shows that the small signal gain coefficients for N_2 molecular dimer at 336.21 nm change with N_2 pressure in the axis direction of the discharge tube when the microwave power is 500 W. It can be seen that there exist gain characteristics when N_2 pressure ranges from 260 Pa to 2200 Pa, and the maximum gain coefficient of N_2 molecular dimer at 336.21 nm is as high as 1.19% • cm^{-1} when N_2 pressure is 1230 Pa. Fig. 5(b) denotes the gain coefficients of N_2 molecular dimer at 336.21 nm measured in the radius direction of the discharge tube when microwave power and N_2 pressure are fixed (The

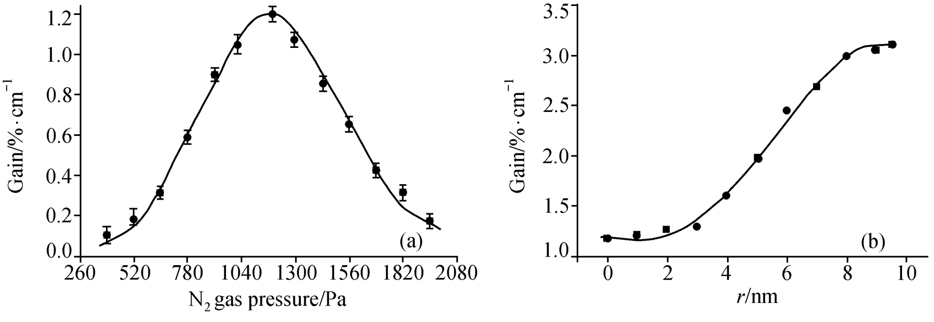

Fig. 5. The gain characteristics of N_2 molecular dimer at 336.21 nm. (a) Relation between gain and N_2 pressure. (b) Gain distributing along the radius of discharge tube.

curve indicates the gain coefficients of N_2 molecular dimer for 336.21 nm increasing in the radius direction of the discharge tube). The reason for this is that the closer these N_2 molecules to the tube's wall, the easier they are excited, so there are more N_2 molecular dimers. Moreover, in order to decide whether the 337.12 nm spectrum affects the gain of N_2 molecular dimer (336.21 nm), their spectral broadened functions were calculated respectively. Their broadening is mainly Doppler effect because the pressure studied is relatively low (260—3000 Pa). Fig. 6 shows the Doppler broadened function of N_2 molecule at 337.12 nm and N_2 molecular dimer at 336.21 nm, and it can be seen that N_2 molecule's 337.12 nm spectrum does not affect the N_2 molecular dimer's gain at 336.21 nm.

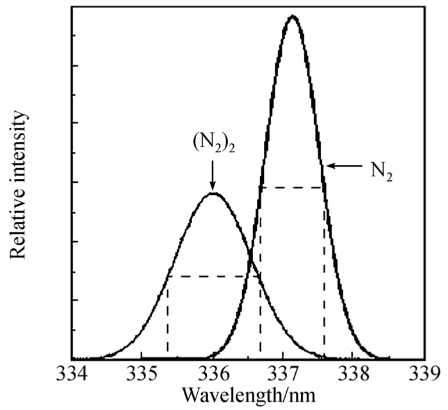

Fig. 6. Broadened Doppler curves for N_2 and $(N_2)_2$.

In addition, the small signal gain of N_2 molecular dimer at 336.21 nm changing with microwave power when the N_2 pressure is fixed is studied. Experimental results show that the small signal gain of N_2 molecular dimer at 336.21 nm increases with microwave power, and when the microwave power is less than 100 W, the gain coefficient is nearly zero, and the N_2 molecular dimer's gain coefficient at 336.21 nm is still not saturated when the microwave power rises to 500 W.

To sum up, when microwave power is greater than 100 W and N_2 pressure ranges from 260 Pa to 2200 Pa, N_2 molecular dimer at 336.21 nm has the stimulated emission characteristics.

3 Conclusion

It is proved that there is N_2 molecular dimer with D_{2h} symmetry group by calculation on the potential energy curves of N_2 molecular dimer belonging to different symmetry groups, and there also exists an electric dipole transition $a^1B_{2g} \rightarrow a^1B_{3u}$ for N_2 molecular dimer with D_{2h} symmetry group. By calculation of the oscillator strength and vibrational frequency, it is shown that $a^1B_{2g} \rightarrow a^1B_{3u}$ is an excimer-like transition. Theoretical calculation of the emission spectra of $a^1B_{2g} \rightarrow a^1B_{3u}$ has predicted that these spectra are located in the range from 320 nm to 440 nm. A series of emission spectra for N_2 molecular dimer are observed experimentally by use of microwave exciting highly pure N_2. The experimental results fit well with the theoretical calculation. The stimulated emission characteristics of N_2 molecular dimer are also studied by the amplified spontaneous emission method. Experimental results show that N_2 molecular dimer has stimulated emission characteristics at 336.21 nm when the microwave power is greater than 100 W, and N_2 pressure ranges from 260 Pa to 2200 Pa. The above work has settled the foundation for studying further laser oscillation of N_2 molecular dimer.

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